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DEVELOPMENT OF BINDER CUM THICKENER *FOR THE* PIGMENT PRINTING USING EMULSION *POLYMERIZATION TECHNIQUE*

A dissertation submitted
In partial fulfillment of the requirement for the award of the degree of
Master of Engineering

In
Polymer Technology

By
Mukesh Dixit
under the supervision of
Dr. A P Gupta
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Department of Applied Chemistry
Delhi College of Engineering Delhi
April 2001

This thesis is dedicated

to my younger brother

Late Yogesh Dixit

CERTIFICATE

This is to certify that thesis entitled " **Development Of Binder Cum Thickener For The Pigment Printing Using Emulsion Polymerization Technique** "Submitted by **Mr Mukesh Dixit** to the Delhi College of Engineering Delhi for the award of degree of **Master of Engineering in Polymer Technology** is a record of bonafied research work carried out by him . **Mr Mukesh Dixit** has worked under our supervision and has fulfilled the requirement for the submission of this thesis , which to our knowledge has reached the requisite standards.

The results contained in this thesis are original and have not been submitted in partial or full to any other University or Institute for the award of any degree or diploma

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CHAPTER 1

GENERAL INTRODUCTION

AND

LITERATURE SURVEY

1.1 Introduction:-

Printing means localized dyeing .Pigment printing conveys applications of finely ground pigment particles on fabric surfaces The origin of textile printing in Asia ,. It is either China or India . Even through from the time immemorial printed fabrics have been produced in India , it is only during the last 60 years that we have adopted to the use of synthetic colors in the printing process In India printing by the use of vegetables dyes is still practiced as in "kalamkari" prints [1] . Synthetic dyes are mainly used for printing of the cotton ,silk , wool etc.

Pigment printing using emulsion either by the oil in water emulsion or the water in the oil emulsion method . This is the major style of printing practiced all over the world and forms more than 50 % of cotton printing . This style has come in vogue after the 1950 s and still holding a predomenant position in the textile printing field The reason for development of this style was limitation in the earlier printing method using direct dyes basic and azoic etc.. of the prints not having the required fastness properties from the consumer angle .

In pigment printing pigment which have no affinity for textile fibers , are fixed on textiles by means of the binding agent [2] The printing paste for pigment printing generally contains (a) pigments (b) emulsifiers (c) thickeners (d)binders (e) softeners (f) antifoaming agents (g) cross linking agents [3]

Binders play an important role in pigment printing . Most of the binders are acrylic based binders . Acrylic ester emulsion polymers serve as binder for woven and non-woven fabrics [4]. A good binder must have the following characteristics [5] .

(i) Good general fastness

(ii) Softness (flexibility of the film)

(iii) Must not cause clogging of screens

(iv) Must have a low electrolyte content

(v) Must ensure a quick washout of screens

Binder is the heart of the pigment printing system which binds the dye to the fabric surfaces after the volatile thickener dried out after . Binder is discovered in 1950 s [6] . An important requirement to be met by the binder system is the good balance between adhesion and cohesion .The binder display the high level of mechanical electrolyte stability for better working result .The commercial acrylic based binders are Tex 2135 (VOCL),) , S.L.N Acramine), Alcoprint PB 55 (allied colloid) etc.

Thickener plays an important role in pigment printing it provides the adequate viscosity for the printing, which restricts the flow of print paste to avoid spreading of colors . Thickener which act as a vehicle for transferring the dyes to the fabric

The natural and modified thickening agents could not give satisfactory results in terms of depth of colors.,brilliance of shades wash fastness and handle of the fabric [6 &7].

Emulsion O/W type thickeners result in good fastness high degree of brilliance and soft handle in the fabric , the use of such a large amount 50 to 80 % of solvent can create some problems .

1. Air and water pollution
2. Wasteful use of energy
3. Explosion hazards

Due to the high vapour pressure of kerosene the printed goods can dried quickly but there is substantial emission of hydrocarbon and carbon mono oxide which pollute atmosphere In India a large quantity of kerosene is imported as it is employed as a fuel in domestic applications Therefore it's availability for the industrial use is restricted The storage of kerosene oil for industrial use increases the fire hazards

In o/w emulsion system kerosene is responsible for attainment of printable viscosity when the print paste is transferred through the screen on the fabric , the o/w emulsion break and separated kerosene spreads and has to be removed during drying and curing This is wasteful use of scarce and imported commodity Due to the severe energy crisis the cost of fuel has gone up and there has been a ten fold increase in the price of kerosene during the last decade

Due to above mentioned limitations of natural as well as kerosene formed synthetic thickeners , there was a need for some safer and easily available synthetic substitutes at a reasonable rate .

At present few indigenous and imported synthetic products are available in Indian markets are carbapol (B F Good rich), Alcoprint P T.F (Allied Colloids)Lutexal H.S F (BASF) These systems have been evolved replacing kerosene partially or completely and are being used commercially

1.2 Acrylic Based Thickeners : -

Acrylic based thickeners are basically copolymers of acrylic acid, meth acrylic by the comonomers proportions polymers having improved properties can be tailored by along with other AA and it's esters The various monomers combination for acrylic based synthetic thickeners detailed in Table 1 .

The acid monomer is responsible for the development for the viscosity on partial neutralization [7 8] Since the pigment print do not require an after wash, the thickener remain on the fabric

Therefore the polymer glass transition temp (Tg) affect the feel of the fabric Acrylate monomers lower the Tg and impart softness [11] Lower the Tg improve the feel of the fabrics but the Tg is to low a value may lead to poor crockfastness For a polymer to be good thickener it is necessary to optimize comonomer composition to get a product with suitable rheologicol properties and Tg

For a good thickener it should exhibit the number of properties given below -

1 High viscosity at very low solid content .

2. Pseudoplastic in nature .

3. Good self life of a print paste.

4. A thickener should be insoluble in water, detergent solution and dry cleaning solvents

Some divalent or trivalent monomers such as divinyl benzene N . methylol methacrylamide ethylene Glycol dimethacrylate etc have been also used as one of the component in producing thickeners . Cross linked polymers can provide printable viscosity at a much lower content (0.5-2 %) . Ref [12] describes that these acrylic thickeners . are two types according to G Kanter.

Alkali soluble :-

These are uncross linked polymers and are called alkali soluble

Alkali swellable :-

These are cross linked and swell in alkali are called alkali swellable

1.3 Polymerization Technique :-

Various techniques are known by which co polymers have been synthesized like emulsion [13] inverse emulsion [14], solution [15] precipatation etc Co polymers in the latex form [16] are effective and easy to use as thickening agents from the application point of view

Powdered synthetic thickeners are very effective but they are seldom used since their applications require an additional step of the acidic from of preparation of an aqueous dispersion of the acidic form of the thickener to develop requisite viscosity. High molecular weight polymers are obtained by the emulsion polymerization . Emulsion latexes are ready to use This technique is superior to others

S. No.	Patent No .	Date	Title	Brief
1	CS268460B1	14/3/1990	Thickening agent for textile printing	No description
2	US3978016	31/8/1976	Pigmentary printing paste for textiles	Aqueous pigment printing ,paste Latex thickener , 30 -50% solid content . 40- 60 % MAA/AA/Crotonic acid , 10 - 30% of Vinyl ester , 50 - 30 % of water insoluble ethylenic monomer.
3	US4085167	18/4/1978	Carboxylic polymeric thickeners	30 % acrylic acid C3-C7 Alkoxyalkyl metacrylate (avr Chain length 6-50 mers)
4	US4509949	9/4/1985	Water thickening agent consisting of co polymers of cross linked acrylic acid and ester	98 9-95 5% of olefinically unsaturated acid carboxylic acids ,1- 3 5 % of an alkylacrylate ester of acrylic /methacrylic acid where in alkyl group contains 10 -30 carbon atoms & 0 1 to less than 1 weight % of a cross linking monomer
5	US5162474	10/11/1992	Synthetic thickener obtained by water - in-oil emulsion polymerization having improved characteristic for the use of textile printing	Olefinically unsaturated acid . multi functional monomer (curing agents) olefinically unsaturated monomer having a nitrile group (acrylonitrile)
6	US5362415	8/11/1994	Acrylic co polymers which is water soluble and moderately water soluable and may be cross linked , and it's uses	Unsaturated carboxylic acid , unsaturated esters oxyalkylated monomer having ethylenic unsaturation and terminated by fatty hydrophobic chain and a cross - linker
7	USRE033008	1/8/1989	Acrylic emulsion co polymers for thickening aqueous systems and co-polymerisable surfactant monomers for use there in	Surfactent monomers ethylenically unsaturated carboxylic acid monomer nonionic ethylenically unsaturated monomers cross linking monomer
8	US4230844	28/10/1980	Processes for the preparation of polymeric thickeners and uses there of	Polymerization carried out in glycol with or without some water unsaturated carboxylic acid , ester with EO groups ending with a hydrophobic group
9	USSR487183	30/5/1973	Printing paste	Composition of printing paste ,combination of poly -acrylamide and monoethanolamine

S. No.	Patent No.	Date	Title	Brief
10	US3915921	2/7/1974	Unsaturated carboxylic acid long chain alkyl ester co polymers and tri polymers water thickening agents and emulsifiers	B.F Goodrich : copolymers of unsaturated carboxylic acid and C10 -30 alkyl acrylate ester (stearyl acrylate)
11	US 3940351	2/7/1974	Polymerisation of carboxylic acid monomers and alkyl acrylate ester in chlorofluoro-ethane	B F Goodrich: acrylic acid . lauryl methacrylate ; polymerisation carrid out in 1,1,2-trichloro-1,2,2-trifluoroethane
12	AUS327856	25/2/1976	Printing of textiles	Acrylic /methacrylic acid ; cross linker (butane diol diacrylatedivinyl benzene,divinyl dioxane);Polymeriasation carried out in castor oil/ isodecyl stearate
13	US931003	4/2/1975	Polymeric soaps	Paint formulation thickened with co polymers of methacrylic acid and stearyl methacrylate
14	GER2534792	19/2/1976	Cross linked ethylene maleic anhydride copolymers	1:1 maleic anhydride and ethylene ;0.3-0 6 mole % triallyl isocyanurate . Useful as thickeners in textile printing paste . Reaction carid out in di-choroethane
15	US3956244	11/5/76	Cross linked maleic anhydride vinyl acetate copolymers and derivatives	Maleic anhydride ;vinyl acetate cross linker (AMA). 0.5%soln of this polymer in water gave viscosity of 200ps (100 rpm) useful in cosmetics
16	GER2204841	16/8/1973	Thickener for pigment printing paste	EO & bis (isocyanatophenyl) methane reaction products as thickener
17	US3894980	15/7/1975	Copolymer thickeners	Copolymers containing Butyl acrylate . di-allyl-phthalate, methacrylic acid , alkoxyethyl acrylate
18	GER2017451	28/10/1971	Acrylic acid -divinyl -p dioxane co polymer	Acrylic acid 96 parts , 90 : 10 % 2,5 divinyl -p -dioxane 2,6 divinyl -p -dioxane;4 parts . reaction carried out in benzene
19	Brit1254743	24/11/1971	Application of dye to napped and pole textiles using a thickening agent	Napped and pile textiles of natural regenerated cellulose , wool ,nylon could be dyed or printed with anionic water sol. Dyes : dispersed metal complex dyes , with water after treatment when polyacrylic or polymethacrylic thickeners were used .Thickener composition AA-EA-MAA-BA
20	GER2123751	2/12/1971	Hydrophilic acrylic block polymers	AA(55)-EHA(10)-MMA(35) block copolymers.1% soln . On neutralizing gave 20 Ps

S. No.	Patent No .	Date	Title	Brief
21	US3878151	15/4/1975	Thickeners for print pastes compossed of cross linked maleic anhydride- alkyl vinyl ether polymers	Maleic anhydrde:vinyl alkyl ether : co-polymerizable monomers cross linked with poly basic amines or polyhydric alcohols / amino alcohols and neutralized with ammonia
22	US3894980	15/7/1975	Thickener	Rohm & Haas: 35 -40% AA/MAA; 20 - 60 % alkoxy , acrylate ,0 8% cross linker
23	US4059552	22/11/1977	Cross linked water swellable polymer particles	DOW : Thickening agent for aqueous dispersion , useful where high shear conditions are encountered , soluble vinyl monomer : cross linker, water in oil emulsion
24	US4138381	6/2/1979	Polymeric thickeners processes for their preparation and uses there of	Unsaturated carboxylic acid ; alkyl acrylate , methacrylate where in alkyl group is up to 30 carbon atoms Reaction medium is glycol and water .
25	US4554018	19/1/1985	Production of polymeric thickeners and their use in printing	Allied Colloid : reverse phase polymerization ethylenically unsaturated acid ethylenically unsaturated acid as it salt with ammonia/amine /alkali metal cross linking agent
26	US4299592	10/11/81	Printing of textile materials	BASF printing formulation ; synthetic thickener: disperse dyes ; N- methylol compound as fixing agents
27	US4190562	26/2/1980	Improved water soluble copolymers of co-polymerizable carboxylic acids and acrylic or methacrylic acid ester	B F Good rich unsaturated carboxylic acid ; acrylic methacrylic ester acrylic methacrylic nitrile or amide; small amount of cross linking agent
28	US4677152	30/6/1987	Polymeric compositions	Allied Colloid ; ethylenically unsaturated monomer containing a pendant hydrophobic group : acrylic methacrylic acid ;EA; acrylamide ; 40 % solid non aqueous dispersion
29	US4849262	18/6/1989	Pigment printing pastes and dyeing liquors containing stable dispersions of finely divided solid poly-isocyanates	BASF ;taxtile materials printed on dyed with this paste possess good fastness properties
30	US4892916	9/1/1990	Polymeric thickeners and their production	Allied Colloid :: Mathacrylic acid ; dialkylaminoalkyl(meth) acrylate or acrylamide ; substantially non -ionic monomer; an allyl ether

S. No.	Patent No.	Date	Title	Brief
31	US 5219969	15/6/1993	Crossed linked polymers with cross linkable groups based on acrylic or methacrylic acid preparation and use there of	BASF 50 -99 parts acrylic /methacrylic acid 1 50 part of N - methylol(meth) acrylamide or derivatives . 50 - 10000 ppm of cross linker 0 -49 part of other unsaturated monomers Water in oil emulsion
32	EP383057B1	3/11/1993	Synthetic thickeners obtained by water in oil emulsion polymerization having improved characteristic for their use in textile printing	Sigma acrylonitrile (0 2 -20%). acrylic acid ,ammonium acrylate Methylenebisacrylamide Water in oil emulsion polymerization

1.3.1 Emulsion Polymerization :-

The mixture of monomers is emulsified in water using specially is selected emulsifiers . Polymerization initiates and other auxaliaries including small quantities of water soluble monomers are then added and the mixture is polymerized at 70 - 90 [17]. The monomer form into droplets which are emulsified by the some of the soap molecules. Excess soap molecules aggregates in to micelles of about 10 molecules in which the polar ends of the soap molecules are turned outwards towards the water, whilst the non polar hydrocarbon ends are turned inwards Monomer molecules like B A , E.A which have low finite solubility in water diffuse through the water and accumulate into the soap micelles and swell them [55]

The polymerization of hydrophilic and hydrophobic comonomer system is not truly emulsion polymerization A two loci polymerization mechanism (18.55) has been suggested i.e the polymerization occurs in water and as well as in micelles and micelles are stabilized by emulsifier [19,20] The initiator decomposes into free radicals which also find their way into the micelles and activate the polymerization of a chain with in the micelle .The product obtained is a colloidal dispersion of the polymer or polymer solutions and is called latex. [21]

The formation of micelles is of fundamental importance in emulsion polymerization [9 22] Latex stability and properties of final products are greatly affected by concentration and the polarity of the monomers [23] and partition of the acid monomers between the aqueous and organic phases

After initiation polymerization inside the micelle swollen with monomers proceed quickly and latex particles grow rapidly The emulsifier is adsorbed on the surface of the growing latex particles are continuously supplied with monomer by diffusion through the aqueous phase from monomer droplets The latter gradually decreases in the quantity as the polymerization proceeds, until a conversion of 80 % approximately. they disappear completely From this point on the monomer in the latex particle is gradually used up and polymerization rate will gradually fall off, polymerization will terminate completely when all monomer in the particle is consumed

The hydrophilic and lyophilic balance indicates the suitability of emulsifier with different system The HLB value of an emulsifier decides its suitability for different systems [24] Particle size is affected by H L B value, if H LB value of the emulsifier in the range of 13-15 particle

size is minimum and emulsion is stable [25] It is reported in ref [26] that particle size increased with decrease in polymerization temperature and decrease in styrene content in the emulsion polymerization of B A , MAA styrene system in presence of sodium dodecyl sulphate emulsifier In ref [27] it is reported that in emulsifier free polymerization of MMA /BA / NaMe increase in BA feed decreases the particle size surface tension and viscosity of the latex but average molecular weight surface charge density and number of particles increases Lin and co workers studied the effect of MMA concentration water /oil ratio and pH on particle size distribution and carboxylic group distribution

The stability of a polymer latex is of prime importance of it any stage of polymerization It is dependent on several factors like reaction rate , temperature , chemical nature and concentration of the monomers , concentration and chemical nature of the surfactants, agitatcor speed and type during polymerization [28]

The colloidal and polymeric properties are not governed by a single component , these are governed by the number of variables which are reported in ref [29]

1 Monomer composition

2 Surfactant system

3 Cross linking / Molecular weight

4 Polymerization process

Elias Unzueta et al [30] describes the colloidal and electrokinetic behavior of poly-methyl meth-acrylate and co-butyl-acrylate (PMMA-BA) latex properties Moreover the use of anionic and non ionic surfactant mixture system may be a powerful tool to ensure the production of m no-disperse latexes Feeney et al [31] explained the function of certain surfactants in obtaining mono disperse latexes as being due to influence of the emulsifier on the reaction kinetics Elias Unzueta and Jacqueline Forceda [32 33] has been describe the effect of mixed emulsifier in seeded and unseeded semi-continuous emulsion co polymerization of methyl meth-acrylate and n butyl-acrylate (BA)

Novak [34] studied the semi batch emulsion co-polymerization of methyl meth -acrylate and butyl-acrylate (BA) The reaction system was stabilized by anionic surfactant Chern and H Hsu [35] has investigated the

effect of the various reaction parameters on the particle nucleation and growth for the emulsion co polymerization of the MMA/BA in a semi-batch reactor .The reaction parameters include the ratio of MMA to BA , concentration of sodium lauryl salphate (S L S) and concentration of nonyl 40 moles ethylene oxide adduct N.P 40 in the initial reactor charge .

Besides the composition of the monomer mixture which is being polymerized , the creation of coagulation is important by other factors e.g. the reaction temp , concentration of monomer mixture in the emulsion being polymerized , the conduction of polymerization , the possibilities of heat removal from the system and the means and intensity of agitation during polymerization .

Water soluble initiators like persulphate , persulphete bisulphite systems and hydrogen peroxide are mostly used as initiator in emulsion polymerization Bovey F A and his co-workers claims that potassium persulphate initiation can be briefly shown as follows [36]

$$S_2O_8^{--} \quad - 2e^- \rightarrow 2SO^0_4$$

The rate of initiation of persulphate is entirely determined by its thermal dissociation

Emulsion polymerization gives polymers of highest molecular weight Final particle size of the product is much smaller then suspension polymerization (50- 500 nm diameter) Emulsion polymerization is a heterogeneous system in which most of the chain propagation reaction ascertains in segregated particles(50-500nm diameter) dispersed in water phase [37]

There are many advantages of the emulsion polymerization over other techniques which are given below

(1) The physical state of the emulsion system gives it is easy to control the process

(2) Thermal and viscosity problems are much less than significant in bulk polymerization

(3) High molecular weight polymers are obtained at even high reaction rate [55]

The product of emulsion polymerization can in some instances be employed directly with out further separation in pigment printing .[7].More over these emulsion systems are environment friendly as they avoid use of toxic solvents

1.3.2 Inverse Emulsion Polymerization -:

The emulsion polymerization of such hydrophilic-monomers acrylic acid (A.A) and acrylamide has been brought out in non aqueous systems in presence of water in oil emulsifier [38] . Such type of technique is known as inverse polymerization it yields a viscous latex consisting of hydrophilic polymer particles swoellen by water in continuous oil phase [17] . Effect of polymerization conditions like pH , monomers and cross linking etc on thickening property of PAA latex has been studied [39].

A poly- acrylic acid thickener synthesized by inverse emulsion polymerization technique with methylene bis acrylamide and hydrophobic monomers having long alkyl groups . Heat sensitive thickeners prepared by this technique from N isopropyl acrylamide with methylene bis acrylamide as cross linking agent in the presence of hydrophobic emulsifier sorbiton mono oleate in hexane [62]. Agglomerated particles can be removed by azeotropic distillation of organic solvents

Inverse emulsion polymerization is not advantageful due to use of costly solvents , conversion of polymer powder in dispersion in aqueous medium and extra cost of solvent recovery step.

1.3.3. Solution polymerization :-

Suspension , inverse suspension solution and precipitation techniques are not much useful in preparation of synthetic thickeners in ready to use form In suspension and inverse suspension polymerization every dispersed monomer droplet acts a tiny bulk reactor These droplets are very active for agglomeration In preventing agglomeration suspending agents , stirrer speed and its design are the key factors .

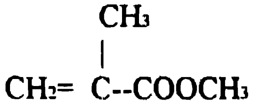
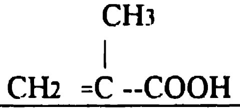
Ref [40] deals with a two step polymerization of MAA/BA system In first step MAA/BA are grafted on butyl rubber using benzoyl peroxide Bz_2O_2 as initiator . This grafted co polymer acts as a stabilizer, for second step where MAA . BA are polymerized in presence of azobis butyro nitrile .In a Japanese patent [41] inverse suspension, polymerization of AA and its alkali metal salt in presence of hydro-phosphorus acid , a nonionic surfactant and water soluble initiator is studied .

Generally solution and precipitation polymerization are not used to develop thickeners, . due to low molecular weight polymers are formed by this technique which leads to poor rheological properties . One disadvantage is the use of solvents like benzene ,toluene and cyclohexane etc. ;Styrene acrylate and ethyl vinyl acetate copolymer emulsions have good thickening effect with PAA thickener ,which is produced by the solution polymerization [42]

In precipitation polymerization of acrylic acid based thickeners organic solution like hexane is mostly used A patent [63] discloses the synthesis of cross linked acrylic acid polymer using the radiation induced inverse emulsion polymerization technique with kerosene as the oil phase .

1.4 Acrylates and Methacrylates polymers and their properties :-

Physical and chemical properties of acrylate and methacrylates are determined by the nature of alkyl group from esterificationable alcohol and the molecular weight of the polymer .the glass transition temperature (T.g) of numerous acrylic homo polymers and formulae of their monomers are given below

Polymer	Monomer formula	Glass transition Temperature(Tg
Polymethyl methacrylate	 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C}{-}{-}COOCH_3$	105
Poly butyl acrylate	$CH_2{=}CH{-}{-}COOC_4H_9$	-55
Poly ethyl acrylate	$CH_2={=}CH{-}{-}COC_2H_5$	-20
Poly meth acrylic acid	 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C}{-}{-}COOH$	128
Poly acrylic acid	$CH_2={=}CH{-}{-}COOH$	106

In case of math - acrylate ester polymers the Tg is influenced by the nature of the alcohol group but also to a lesser extant by stereo regularity of the backbone chain . Glass transition temperature affects the mechanical and other properties over a specified temperature range .

Below the Tg polymers are stiff ,hard ,brittle and glass like, above the Tg polymers are soft and limper in nature , they flow and are tacky even at higher temp Polymerization of two or more monomers may regulate the Tg of a polymer, the approximate value of a copolymers can be calculated from the knowledge of the weight fraction of the monomer type and the Tg of each homo polymer by the following equation

$$1/Tg = W1/ Tg1 + W2/Tg2 \text{---------------} Wn/Tgn \ .$$

Suitable properties of a polymer can be obtained using mixture of monomers PMAA is hard and has no tack at room temperature ,while PBA, is softer and much tackier [55]

1.5 Rheological nature of synthetic thickeners :-

Knowledge of the flow behavior and mechanism of viscosity development is of fundamental importance for thickeners used in textile printing Acrylic based thickener contain co monomers having carboxylic groups (-COOH) . Viscosity of these thickener is very low in acidic medium because of polymer chains are randomly coiled and their average distance is low . In the aqueous solution of these synthetic thickeners viscosity develops immediately after neutralization of carboxylic acid and or maleic anhydride . Due to the carboxylate ions formed after neutralization carrying negative charge on them , electrostatic repulsion develops, polymer chains uncoiled . This leads to increase in viscosity by uncoiling of polymer chains and increase in a average end to end distance [9,10]

Several inorganic bases like ammonium hydroxide , sodium hydroxide , potassium hydroxide and sodium bicarbonate and organic bases like ethanolamine , morpholine and alkyl amines have been used for neutralization of synthetic thickeners [12] Ammonium hydroxide is most commonly used base for the thickeners used in pigment printing., because it evaporates during curing .

Viscosity is the prime , importance for the synthetic thickeners which depends upon certain parameters .It is a complex process.

I Co polymer composition

Ii Gel contents and cross linking agent

iii Solid content

IV pH

V Shear rate

Vi Concentration of electrolytes presents

1.5.1 Co polymer Compositions :-

Composition of copolymer affects the viscosity after neutralization. Viscosity of the synthetic thickeners depends upon the amount of carboxylate ions. Bajaj and coworkers [43] observed that Brookfield viscosity of MAA/EA copolymer neutralized with NH4OH increases with increase MAA fraction in the copolymer , but after certain value viscosity decreases with increase MAA fraction due to increase in glass transition temperature (Tg) of the copolymer with increase MAA in the copolymer .

The hydrophobic comonomer ethyl acrylate lower the Tg and hence contributes to the softer handle and indirectly to viscosity development .In BA/MAA co polymer [64/32 %] observed that partial replacement of B.A by EA takes place viscosity is increased suddenly from 110 poise to 610 poise [3.6% solid] .Hence it is necessary to optimize the co monomer ratio for the maximum viscosity

1.5.2 Gel Content and Cross Linking Agent :

There are some divalent / trivalent monomers such as methylene bisacrylamide , allyl meth acrylate etc have also been used as one of the monomer producing synthetic thickeners loosely cross linked copolymers give adequate viscosity at lower solid content [0.5 to 2.0 %] . The degree of cross linking and gel content are related with each other When more is the cross linking density , more is the gel content and more is the viscosity after neutralization EA /BA/MAA ter polymer . In ref [43] Brookfield viscosity increase linearly with gel content was observed for MAA/ EA copolymer with ethylene glycol di mathacrylate [E.G.D.M.A] N -N methylene bisacrylamide (MB AM) as cross linking agent Gel content and degree of cross linking increases with concentration of cross agent in the feed up to a certain value and then decreases This happens due to intermolecular cyclization where a pendent double bond of growing polymer radical cyclizes with it's own chain

1.5.3 Effect of Solid Content :

Solid content is the more in emulsion more is the viscosity . Ref[9] indicates that a very high viscosity is obtained at very high solid contents because of polymers chains are closely packed together and very less free solvent remain between them

1.5.4 Effect of pH on viscosity :

Viscosity depends upon pH . When NH4OH is added to polymer emulsion , some ionization occurs providing [NH_4+] is added to polymer emulsion , some ionization occurs , giving [NH_4+] ammonium counter ions and polymeric chains COO- ions .When complete neutralization is achieved , further addition of ammonia results in a build up of NH_4+ counter ions leading to decrease in ionization of - COOH group by law of mass action and common ion effect . Recoiling of expended chains starts and viscosity decreases . Measurement of viscosity over a wide range is carried out in ref [43] . In a EA.MAA co polymer cross linked with divinyl benzone it was observed that the viscosity increased from 60000 cp at 7.6 to 240000 cp at pH 9.4 [44]. Therefore optimization of pH range is necessary to get the maximum viscosity .

1.5.5 Effect of Shear Rate :

Synthetic thickeners are pseudoplastic in nature i.e. their viscosity decreases with increase in shear rate , which is ideal for printing paste for example saponified acrylonitrile terpolymer [45] had a viscosity of 1625 cp at 6 rpm , on increasing the rpm to 60 the viscosity decrease to 1300 cp . The observe drop in the viscosity values with increase in shear rate may be related to the break down of the hydrate or solvent enveloped network polymer in the dispersions , by mechanical action which change in structure from gel to sol [46] .According to Kdlickeetal , subjecting the polymer solution to mechanical stress wooed separate loosely linked polymer chains and hence viscosity decreased [46]

1.5.6 Effects of Electrolytes :-

A drop in viscosity was observed when ions added in the form of salt e.g ammonium sulphate diammonium phosphate etc[47]. On addition of 1 0 % NaCl to a 4 0 % solution of saponified poly acrylonitrile, Brook field viscosity at 6 rpm was reduced to 5000 cp from 8000 cp .Brook field viscosity (at 20 rpm 20 centigrade) of printing paste of containing acrylic thickener reduced from 25000 cp to 15000 cp upon addition of 0.1% solution of sodium sulphate [48]

In ref [43] Chavan et al found that cross linked polymers are more sensitive to electrolytes than uncross linked polymers . Electrolytes or salts which are added externally decrease dissociation by common ion effect and particle precipitation of chain occurs resulting in the drop of viscosity .

The reason could be that in case of cross linked polymer desorption of observed vats from polymer network occur due to recoiling of polymer chain , so polymer chains are no longer in a swollen form leading to dramatic drop in viscosity . In case of un cross linked polymers though the polymeric chains recoiled but they remain in the dissolved state , so the drop in viscosity is not high as cross linked polymers . Uncross linked are less sensitive then cross linked due to high solid content .

1.6 Performance of Acrylic Based Thickeners:-

A Japanese patent [49] reveals the use and performance of MAA.EA BA polymer (68 : 5 : 15) cross linked with butane diol acrylate in printing cotton fabric with 5.0 % Ryude w Tarquoise Blue F.B. The printed fabric was cured at 150 for 3 minutes and the prints obtained had good color fastness and handle . Methacrylic acid butyl acrylate polymer with ethylene glycol dimathacrylate [EG.DM] as cross linking agent have found effective use , in print paste formulation containing reactive acid and metal complex dyes and also with pigments .Uncross linked MAA.B.A copolymer has been used for the printing of non woven napped polyamide carpeting acid dye . Methacrylic acid butylacrylate methyl methacrylate ter polymers also have been used in pigment printing for partial substitution of solvents . These terpolymers have good electrolyte resistance (50)

In ref [51] it is reported that printing on viscose by synthetic thickener with C.I reactive red 218 gave better color fastness and tristimulus value than natural alginate thickener but give poorer dry and wet rub fastness In ref [52] it is reported that copper phthalocyanine pigment was tried with thickener Of MAA/BA / Vinyl acetate [41 : 42 : 14] copolymer on cotton staple fiber viscose polyesters and silk . After dying at 50 ^{oC} fabric and thermoset at 140 ^{oC} . Print performance was claimed good in order of brightness colouristic yield , good leveling , and sharp out lines .

A thickener prepared by inverse emulsion technique was used with reactive dyes [6,4]. Co polymer was composed of AA stearyl methacrylate with cross linking agent allyl pontaerythritol .In ref (48) it is reported that prints with

bright color ,sharp contour lines were obtained by acrylic acid acrylamide thickners with blue halizarine RT (BASF). After printing textile was left for 120 seconds and then dried at 150 °C for 150 seconds [64] BASF thickener based on acrylic acid acrylamide acid copolymer with a plasticizer (polydemethyl siloxane) was tried with blue pigment C.I 174160 ON viscose staple yarn fabric . Drying and fixation were done at 110 °C and 150 °C respectively with dry air . Printed with the aid of flat screen brilliant blue print with high levelness sharp out lines soft handle were claimed.The dry and wet crookfestness were claimed 4 and 5 respectively while wash fastness was claimed 4 according to standard scale of rating [64] .

In the patent [53] claimed that a thickener based on emulsion polymer of MAA/AA/allyl ether [50:40:10] was used with impreron blue KRR [TM] and halizarine borde aux on 50/50 polyester cotton blend .The print was dried and cured at 150 °C for five minutes .Excellent color yield , brightness and sharp contour are obtained

A modified polyacrylic acid thickener which reduced urea consumption to 50 % of BOD lavel did not interfere with dye fibre fexiation reaction and saved 30 % dye stuff with brilliant color development [66] . In ref [48] it is claim that printing was done with phthalocyanine preinone thio indigo pyrrol ,pyrroledone ,and anthraquinone dyes .Printing with an azo dye with acrylic based thickener gave a golden yellow printing fast to light 'sublimation and dry cleaning

1.7 Binders :

Binders are usually resin in water dispersion . These products under the effect of the temperature and pH cross link in the way that they result in a " Plastic " film which bonds the pigment to the fabric surface

1.7.1 Composition of binders :

Binders are the ter polymer of styrene , acrylics and their esters of varying ratio with acrylamide etc . Acrylic type binders have good general fastness but have the disadvantage of providing harsh prints . Binders on acrylate basis e.g Alcoprint [PBA] have 10-20 PPM formaldehyde . Some binders consist of acrylamide with styrene e g. tex 2149[5] Butadiene type binder's mainly consists of butadiene mainly These are obtained by the blending in various ratios of the acrylics and butadiene .Self thickening binder exhibits two segments one is the soft sigment BA,EA,etc and second sigment is the acid like AA,MAA, which is responsible for development of viscosity .

1.7.2 Mechanism of binder in pigment printing :

Mechanism of the binder is complex , perhaps it is as follows The binder is expected to form a transparent film , which entraps the pigment particles and binds the same to the fabric substrate . Print pastes which are applied in an unpolymerized state at the fabric at the time of printing but is polymerized or cured as the acid donor , the catalysts splits at high temperature of 140 to 150 °C giving the acid to the system and vaporizing the ammonia content of the catalyst [54] where by the binder gets polymerized into a long chain molecule which is transparent and insoluble .This gives the necessary brilliancy to the prints and the required fastness to wet and dying rubbing . The curing temperature by dry air and is kept at 140 to 150 °C and the time of contact with the hot air at 3 - 5 minutes

In kerosene emulsion diammonium phosphate $(NH_4)_2HPO_4$ is added as a catalyst for fixation of binder like N methylol methacrylamide with hydroxyl groups of cotton This fixation occurs in a acidic pH [54]

$$\text{Binder -}CH_2OH + HO \text{ -- cellulose} \xrightarrow{\text{DAP pH- 3}} \text{Binder -}CH_2O \text{ - cellulose} + H_2O$$

$$(NH_4)_2HPO_4 \longrightarrow 2NH_3 + H_3PO_4$$

(DAP)

Ammonia goes away and phosphoric acid gives required pH But in case of synthetic thickener on neutralization (with ammonia) ammonium carboxylate ions are formed during paste formation , liberate ammonia during curing and lowers the pH, fixation of binders occurs

1.7.3 Performance of Binder :

Selection of binder in the pigment printing is very critical from the performance point of view . Binder affect the pigment printing in great extent .In pigment printing binder imparts crisphandle and brightness to the print with excellent wash fastness .Butadiene binders although they have a very soft handle and better dry rubbing fastness are used in lower quantity since they are not only more expensive than the acrylic ones but also because under the influence of light and temperature have the tendency to yellow . Thus causing change of the shade of the prints [5] .In case of pigment printing on towels the use of a butadiene binder is essential when printing on knit wear the use of butadiene binder is recommended [5].

Acrylamide moieties could be present in the binder or thickeners Alcoprint's binders are how ever completely free from acrylamide Main sources of fixing are the binder and pigment dispersions Binder on butadiene basis are naturally free from formaldehyde , commercially available binder alco prints [PB55] is free from formaldehyde [66].Electrolyte stability is an important property of a print paste .It decides the effect on viscosity of paste on addition of electrolytes such as binder , pigments and reducing agents . For deep shade additional binder is required , additional thickeners may need to be added [68]

Fastness properties are determined by pigment and binder ratio ,poor coulor to binder ratio if the dye concentration is more and the binder concentration is less, it results in poor fastness . For an ideal fastness keeps the color to binder ratio at 1.3 and in rare cases 1 : 4 .The low concentration of dye can give good results even at a low binder concentration of 7 to 6 % . The pigment emulsion should be necessarily pasted with the extra binder ,before addition to the reduction thickening this ensures each particle of dye stuff getting a coat of binder film to ensure good fastness on curing[67] Print Rite binder 594 is one of recently introduced binder by BASF It exhibits good crock fast ness wet and dry both , wash fastness properties rating is 5 , out standing redispersibility , very soft hand , superior color value , electrolyte stability and good print paste stability [70] Binder should display good mechanical property Acramine SLN(CCL) binder exhibits fidelity of color (there should be no shift in wave length of maximum absorption of the color) with RAN 5000 thickener and good compatibility with all synthetic thickeners The cross linked thickener also contain inherent acid i e aluminum sulphate which may help in the fixation or polymerization of binder film[69]. The attempt to check the effectiveness of this acid showed that washing and rubbing fastness was very good even in the absence of the acid catalyst , it is the combined effect of binder with catalyst, on print performance

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Chapter 2

Synthesis and Characterization Of

BA EA MAA

Copolymers & Ter polymers

Cross-linked with N Methylol methacrylamide(MIMAM)

2.1 Introduction :-

Co-polymers of hydrophobic monomers like butyl acrylate, ethyl acrylate ,styrene and small amount of AA,MAA and maleic anhydride are used as thickeners . Some terpolymers which are used as binders based on acrylates. Those products have the interest for last two decades for replacement of kerosene in pigment printing . Self-thickening binder for pigment printing concept is totally neglected in Indian textile industry . Self thickening binders are the ter polymer. Such type of product has lot of interest at this time to eliminate the separate use of thickener in pigment printing. **Our man approach to develop a Binder cum Thickener for pigment printing to avoid the use of separate thickener.**

2.2 Experimental :

2.2.1 Materials :

Methacrylic acid , butyl acrylate , ethyl acrylate (provided by **Vam organic and Chemicals Ltd**) were used as comonomers . A combination of anionic surfactant (sodium lauryl sulphate , Qualigens fine Chemicals) and an ammoniated sulphonic acid Spectra [S 301] and a nonionic nonylphenyl ethylene oxide condensate (Alfox 200) were used as emulsifier. N Methylol meth acrylamide and potassium per sulphate [**Central Drug House Pvt Ltd (C.D.H)**] were used as cross linking agent and initiator respectively . Sodium bicarbonate (C.D.H) was used as buffer .

2.2.2 Polymer synthesis :

Butyl acrylate (B.A) ethyl acrylate EA & methyacrylic acid copolymers and ter polymers were synthised with varying amount of N Methylol methacrylamide (2.5 to 4.0 % wt % of total monomer) by semi continuous emulsion polymerization technique . The recipe of 980 grams batch is given in table 2.1

Table 2.1

Compound	Weight (g)
Butyl acrylate	140 -311
Ethyl acrylate	100 -243
Methacrylic acid	54 -122
N Methylol methacrylamide	10 - 18.75
Sodium lauryl sulphate (S.L.S)	1.3-1.5
Spectro S 301 (anionic surfactant)	18-24
Alfox 200 non ionic surfactant	2-6
Potassium persulphate (KPS)	2.04 -2.5
Sodium hydrogen carbonate (S B.C) (buffer)	0.1 -0.250
Water	450 -470

Feeding time	3.00 hours
Holding time	1.00 hour
Reaction temp.	76 to 80 °C

240 grams of deionized water , 0.89 grams sodium lauryl sulphate and 0.250 gram sodium hydrogen carbonate were taken in a reactor of two liters capacity All the monomers were taken in a monomer tank , 0.3 gram S.LS , 5.0 gram Alfox 200 and spectra S 301 16.0 gram were also added in monomer tank with 200 gram denionized water . Monomers are pre emulsified by the help of high-speed lab stirrer.

The reactor was equipped with a mechanical stirrer , a condenser , a thermometer and two dropping funnels for monomer emulsion and initiator feeding , 2 5 gram KPS was dissolved in 60 gram deionized water. Initial feeding was done with 1/2 part initiator solution and 50 gram pre-emulsified monomer to allow the build up of particles with higher molecular weight . The rest emulsion monomer and initiator were feed continuously in three hours

2.2.3 Polymer Characterization :

2.2.3.1 Acidimetric titration :-

Concentration of free MAA in these terpolymers was determined by acidimetric titration of 0 5 % solution of these polymers in methanol against standard NaOH with phenolpthlein as indicator .

2.2.3.2 Infra red analysis .:

I R Spectra of MAA - B.A - EA co polymers and ter polymers were record in KBr pellets using Nicolet EPX 400 FTIR (MODEL) Pellets were obtained by grinding 5 mg of samples with 5 mg of KBr in a mortar and then compressed to get a pellet .

2.3 Results and Discussion :

2.3.1 Acidimetric Titration .:

When solution of these uncross linked terpolymers in methanol was titrated with standard NaOH solution MAA content was found much less than amount of MAA incorporated in feed (table 2 2) , though the conversion in each case was found around 95 % In the case of polymers having high molecular weight , not all carboxylic acid groups are available for neutralization , due to their presence in deep core of the particles (71) . If sufficient time is given all of them will be neutralized , but hydrolysis of the ester group may occur to give highest value

Table 2 2

Polymer code	Feed concentration Wt %			MAA in terpolymer (Acidimtric titration)	Yield %Wt
	BA	EA	MAA		
BCT 8	39.13	27.4	33.4	31.84	95 3
BCT13	38.14	38 96	22.88	22.01	96 2

2.3.1 I .R Studies :

Absorption bands in the I R spectra of the copolymers and ter polymers have been assigned by comparison with the corresponding homopolymers given in reference (43)

Table 2.3 Characteristic I R Frequencies of polymethacrylic acid (PMAA) , poly butyl acrylate (PBA) and poly Ethyl acrylate (PEA) .

Polymer s	Wave number cm-1	Intensity	Assignments
Poly methacrylic acid	3419-3512	Broad	O-H stretching vibration of MAA
	2960-2870	Weak	C-H stretching vibration
	1700	Strong	Carbonyl stretching vibration of acid group of MAA
	1485	Strong	C-H deformation of - CH2 group
	1450	Strong	C-H deformation of (Asymmetric) of CH3 of MAA
	1390	Medium	C-H deformation of (Symmetric) of CH3 of MAA
	1270-1180	Strong	C-O stretching vibration of - COOH of MAA
	987-947	Weak	- OH out of plane of deformation of MAA
Poly Ethyl acrylate	2960-2850	Weak	C-H stretching vibration
	1740	Strong	Carbonyl stretching vibration of ester group of EA
	1450	Medium	C-H deformation of CH2 group
	1250-1170	Medium	C-O stretching vibration of -COOC2H5 group of EA
	1040	Weak	C-O-C stretching vibration of EA
Poly acrylate	2960-2860	Weak	C-H stretching vibration
	1740-1700	Strong	Carbonyl stretching vibration of ester group of BA
	1470-1450	Medium	C-H deformation of CH2 group
	1250-1170	Medium	C-O stretching vibration of -COOC4H9 group of BA
	1060-1040	Weak	C-O-C stretching vibration of BA

Table 2.4 Characteristic I R Frequencies of MAA - EA -BA co polymers and ter polymers

S.No	Wave number		Assignments
	cm-1	Intensity	
1	3460--3207	Broad	O-H stretching vibration of MAA
2	2959	Strong	C-H (asymmetric) stretching vibration of - CH3 group of MAA
3	1734.4	Strong	Carbonyl stretching vibration of ester group of BA & E
4	1704.3	Strong	Carbonyl stretching vibration of acid group of MAA
5	1515.5	Strong	C-H deformation of - CH2 group
6	1451.7	Strong	C-H deformation (Asymmetric) of -CH3 group of MAA
7	1383.8	Medium	C-H deformation (Symmetric) of -CH3 group of MAA
8	1257-1168	Broad	C-O stretching vibration of -COOH of MAA & COOCH2 - of BA & EA
9	1065-1025	Weak	C-O-C stretching vibration of BA & EA
10	943	Weak	-OH out of plane deformation of MAA

In the I R Spectra of the co polymers and ter polymers, broad bands are observed in 3460 - 3207 cm-1 due to O-H stretching vibration of -COOH group of MA A & strong bands at 1704.3 cm-1 due to carbonyl stretching vibration of caboxylic acid groups (figure 2.1 - 2.2). A sharp peak was observed at 2959 cm-1 due to C-H asymmetric stretching vibration of CH_3 group of MAA . In I R Spectra a sharp peak was appeared at 1734.4 cm-1 due to carbonyl stretching vibration of ester group . At 1024.6 cm-1 and 1026.4 cm-1 weak peaks were observed due to C-O-C stretching of the ester group (fig. 2.1- 2.4). These peaks are also characteristic of PBA and PEA.

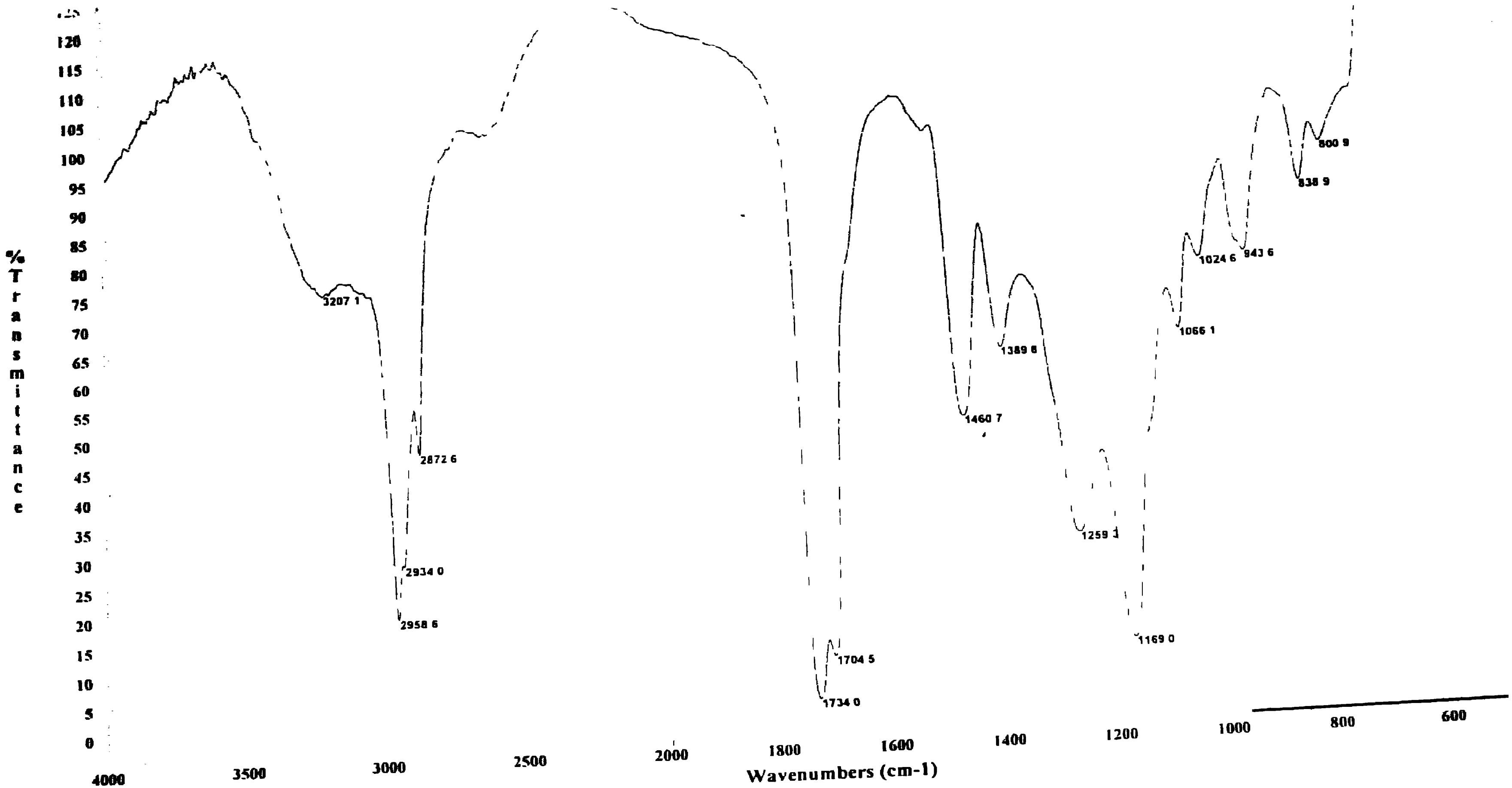
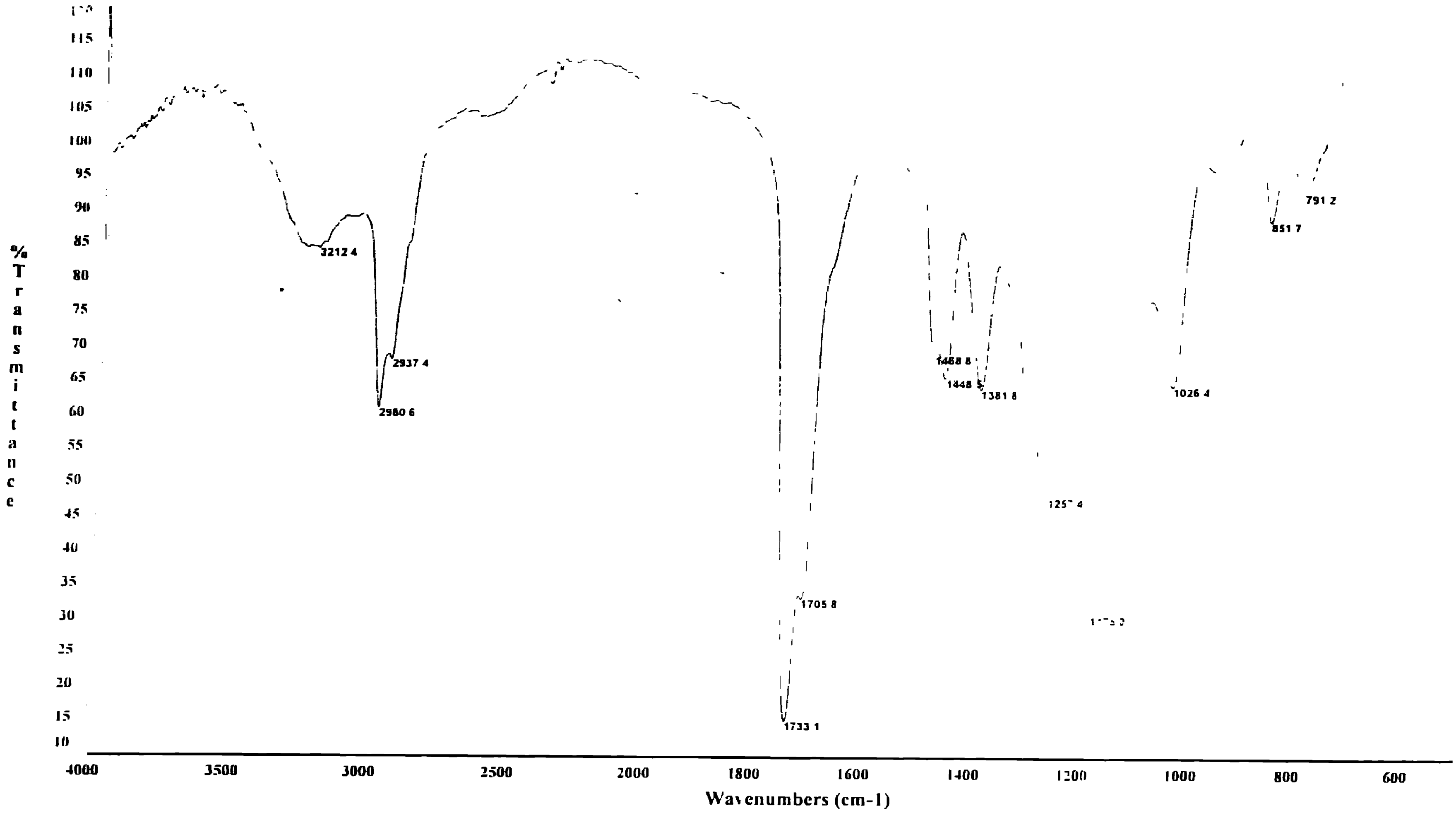


Fig 21 BCT-9

Date: Mon Feb 12 11:27:42 2001

Scans: 4

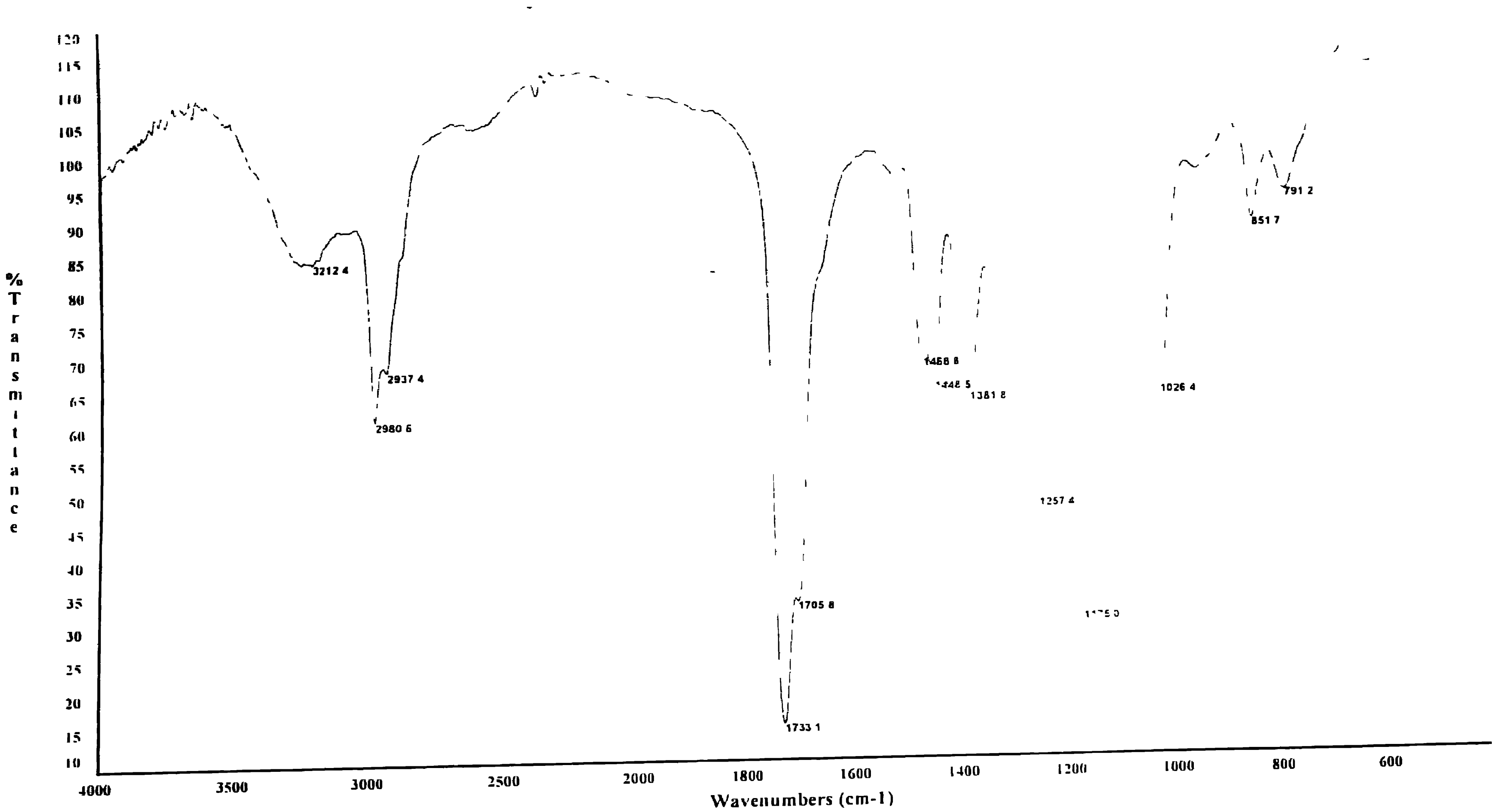
Resolution. 4.000



Date: Mon Feb 12 11:22:52 2001 Fig 2.2 BCT-12

Scans: 4

Resolution: 4.000



Date: Mon Feb 12 11:22:52 2001

Fig 22

BCT-12

Scans: 4

Resolution: 4.000

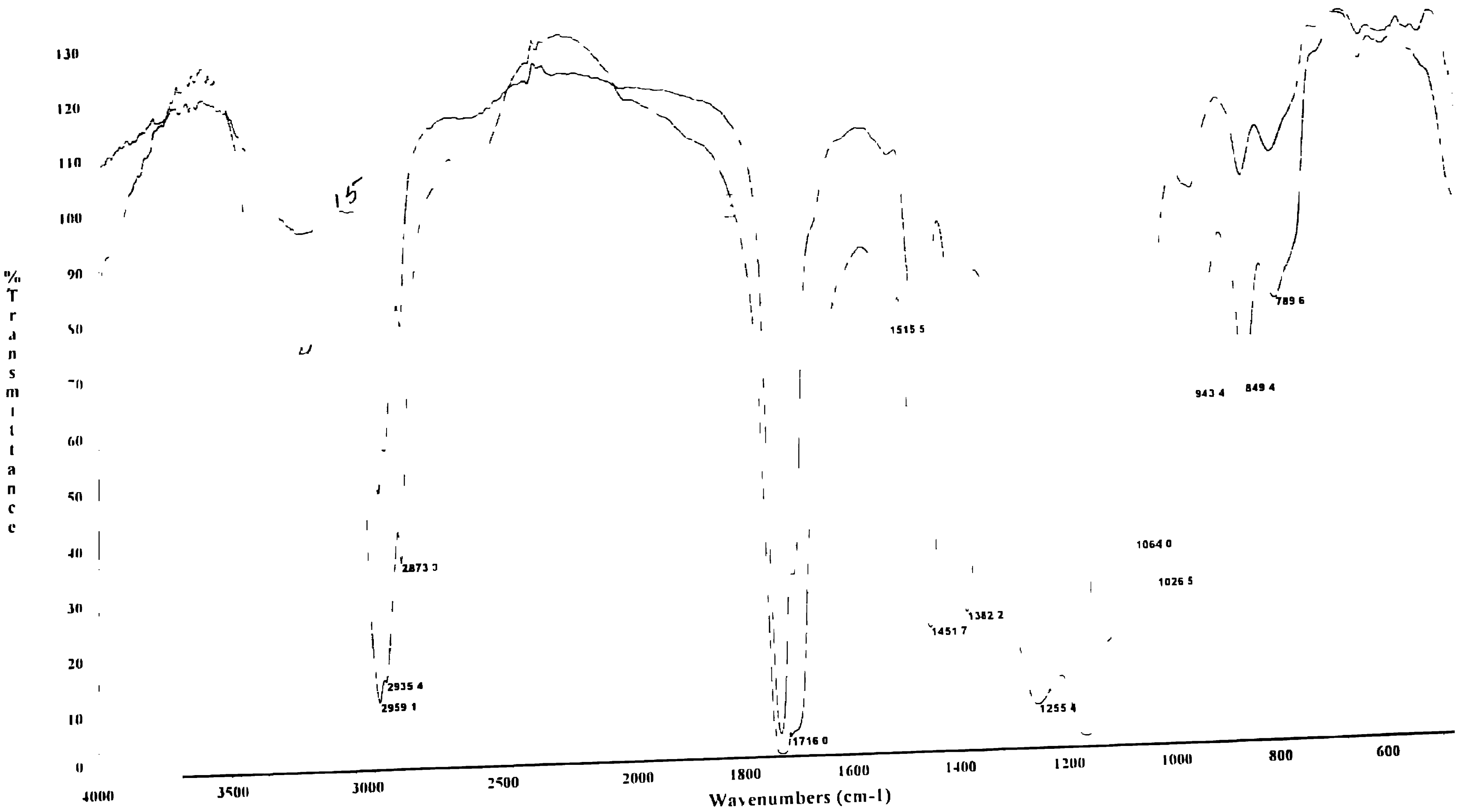


Fig 24 BCT-14 and BCT 15

Date: Mon Feb 12 11:03:56 2001

Scans 4

Resolution 4.000

Chapter 3

Rheological

Studies

3.1 Introduction :

Importance of the viscosity or flow of a print paste is always emphasized because it affects the amount of paste applied as well as the spread of paste on the surface and into the structure of the textile material [56] . Printing operation of such type of thickener is decided by the flow behavior of the thickener employed to prepare the printing paste

Dynamic viscosity (η) of fluids is defined as the ratio of shear stress τ and shear rate

$$\eta = \tau / \gamma l$$

if η is independent of shear the liquid is newtonian like vesitable oils , lumbricating oils . Polymer melts and solutions generally show deviations from the newtonian flow , they are known as non newtonian fluids . Their flow behaviors depends upon shear rate Their viscosity decreases with increases shear . Thickeners are shear thinning in nature and hance posses pseudoplastic flow behavior . This can be described by Ostwold de wale power law equation [57] .

Equation

$$\tau = K \gamma^{n}$$

where τ is shear stress γ is shear rate , K is a constant and n is power having value 0 to 1

3.1.2 Chemical Structure and Rheology of Synthetic Binder Cum Thickeners :

Synthetic thickeners are high molecular weight polymers (mol.wt 300000 to 500000) containing an acid monomer which is a major component responsible for viscosity build up . They form a type of spatial lattice in the aqueous medium due to their moecular size and chain networks which restricts the normal flow of solvent Kerosene emulsion thickeners used in pigment printing is oil in water type [O/w] .Oil is present in dispersed phase and water is dispersion medium . Development of viscosity occurs due to the difficulty of the oil droplet movement present in the dispersed phase [58]

3.2 Experimental :

3.2.1 Gel Content Determination :

Gel content of the cross linked polymers was measured gravimetrically [59] Polymer emulsion was broken by 15 % sodium chloride solution adding to it The solid polymer was washed several times with deionised water and finally with cyclohexane , dried it at 60 °C for 24 hours in vacuum oven

5 0 gram solid polymer was mixed with 100 ml of methanol and kept 40 ^{oC} for 48 hours After it the mixture was centrifuged at 15000 RPM at room temperature using Remi research centrifuge, the swollen to remove the solvent centrifuged again The gel was then dried in a vacuum oven at 60 ^{oC} for 24 hours and weighed

Gel content = weight of centrifuged polymer X 100 / 5 0 (weight of solid)

Flow properties of thickening agents were measured with the help of Brookfield RVDT digital viscometer Viscosity was measured with respect to concentration of the thickener, shear rate and pH of the medium

3.2.2 Polymer concentration :

Polymer emulsion having 40 0 % solid content was diluted to 1 0 to 4 0 % for cross linked polymers and viscosity was measured

3.2.3 Shear Rate :

Brookfield viscosity at 2 5 to 100 rpm was measured to study the effect of shear rate at 4 0 % solid for cross linked and 8 0 % for uncross linked polymers

3.2.4 Effect of MAA :

On increasing MAA content viscosity increases with certain degree shown in table 3 1

3.2.5 pH of the medium :

As the viscosity in the pH range of 7 to 7.5 is important for pigment printing the viscosity measurement carried out at different pH [7- 10.5] values . The concentration of the binder cum thickener chosen for studying the pH dependency was 3.6 % for the cross linked and 8.0 % for uncross linked polymers

3.2.6 Storage Time :

For the commercial feasibility of binder cum thickener , the storage stability for several days is required prior to use Keeping this in mind , the viscosity was measured at 24 hours interval for 7 days .

3.3 Result and Discussion :

3.3.1 : Brookfield viscosity of co polymers and ter polymers of MAA BA & EA

These polymer emulsions BCT 2 to BCT 17 having solid content 40 ± 1 % and pH 5 ± 0.1 were diluted and pH was raised to 5 5 to 9 5 by adding ammonia . Then Brookfield viscosity was measured at 20 rpm at room temperature (table 3 1) The viscosity of carboxylated latex on neutralization increases with

1 Increase in -COOH acid content of the polymer
2 With the decrease in Tg
3 With an increase in hydrophobisity of the comonomer

Brook field viscosity of the uncross linked polymers was lower than cross linked polymers (table 3 1) BCT 2 to BCT5 were found unsuitable for thickening applications , because the solid content is too high to be used in pigment printing can be seen in (table 3 1) BCT 15 is the best binder cum thickener , it shows brook field viscosity 130 poise (C=3.6%) in (table 3 1) . Its rheological properties were also studied .

Table 3.1 Brook field viscosity of co polymers and ter polymers of MAA -EA - BA .

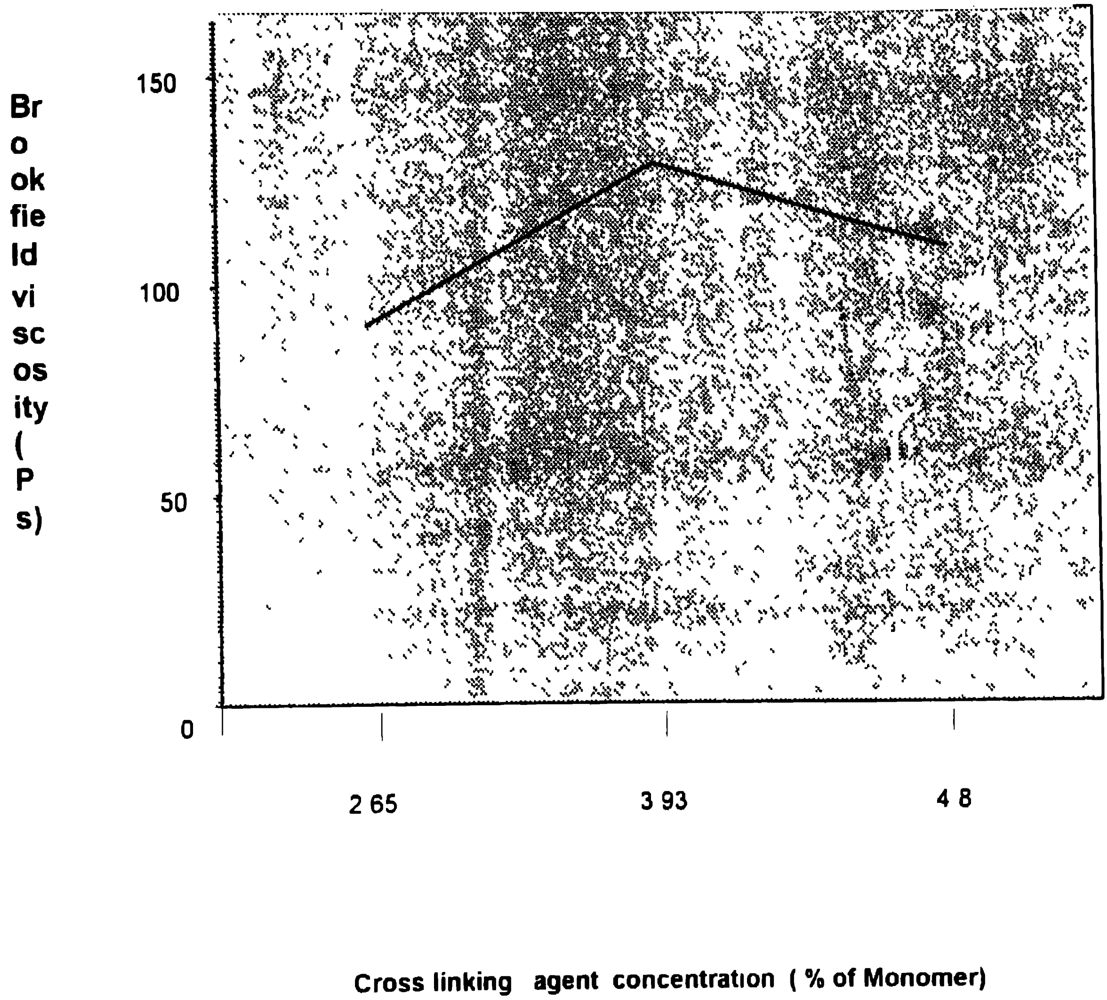
Table 3.1

S. No.	B.A W.T	E A WT%	MAA WT%	Methylolmethacryl amide WT%	Brook field viscosity in poise	Polymer code
1	82.89		14.39	2 8	36 PS (C = 12 0)	BCT 2
2	80.05		16.38	3.56	154 PS (C =12.0)	BCT 3
3	74.4		21.55	3 56	170 PS (C =10.0)	BCT 4
4	69 48		26.94	3.56	225 PS (C =8)	BCT 5
5	64.2		32.2	3.56	112 PS (C =3.6)	BCT 6
6	64.2		32.2	3 56	140 PS (C =3.6)	BCT 9
7		64.2	32.2	3 56	128 PS (C =1.8)	BCT 10
8		64.2	32.2	3 56	129 PS (C =1.8)	BCT 12
9	37.63	26.3	32.2	3.96	180 PS (C =2.8)	BCT 7
10	39.13	27.4	33.4	NIL	42 PS (C =2.8)	BCT 8
11	37.13	37.93	22.28	2.65	82 PS (C =3.6)	BCT 16
12	36.64	37.43	21.93	3.93	130 PS (C =3.6)	BCT 15
13	36.29	37.07	21.75	4.8	106 PS (C =3.6)	BCT 14
14	38.14	38.96	22.88	NIL	20 PS (C =3.6)	BCT 13
15	36.6	37.4	21.9	3.93	128 PS (C =3.6)	BCT 17

3.3.2 Gel Content Of Cross Linked Polymers :

The degree of the cross linking of the ter polymers is determined from gel content of the ter polymer table (3.2) it was found that gel content increases with increase in the amount of cross linking agent methylol methacrylamide in feed up to 3.9 % by wt% and beyond that the gel content decreases **(fig 3.1)**

fig(3.1) Variation of Brookfield viscosity with cross linking agent concentration in monomer field



Polymer code	**BA wt%**	**EA wt %**	**MAA wt %**	**Methylol methacrylamide**	**Gel content (%)**
BCT 13	38.14	38 96	22.88	NIL	-
BCT 14	36 29	37 07	21.75	4 8	76
BCT15	36 64	37.43	21.93	3.93	85
BCT 16	37.13	37.93	22.28	2.65	69
BCT 17	36.6	37.4	21.9	3 93	83 5

In ref [43] the effect of different cross linking agent on the gel content has been studied in detail . When cross linking agent is present as a comonomer two types of reaction take place

(i) Inter molecular cyclization Where a pendent double bond of growing polymer radical cyclizes with it's own chain

(ii) Inter molecular cross linking which takes place between a growing radical and the polymer chain having unreacted double bonds

On increase in amount of cross linking agent intra molecular cross linking increases leading to it's less availability for inter molecular cross linking [60]

3.3 .3 Brookfield Viscosity Of Cross Linked Polymers.

Brookfield viscosity of all the cross linked polymers (3 6% solid content) was measured at 20 rpm and pH 8 5- 9 5 , in the cross linked polymers very high viscosity was obtained at much lower solid content in comparison to un cross linked polymers Brookfield viscosity increased linearly with increase in gel content of the cross linked polymers **(table 3.3 fig 3.2)**

Polymer code	Gel content (%)	Brook field viscosity (ps)
BCT 13	-	20
BCT 14	76	110
BCT 15	85	131
BCT 16	69	90
BCT 17	83 5	127

fig (3.2) Plot of gel content vs cross linker (MIMAM) feed concentretion (wt%)

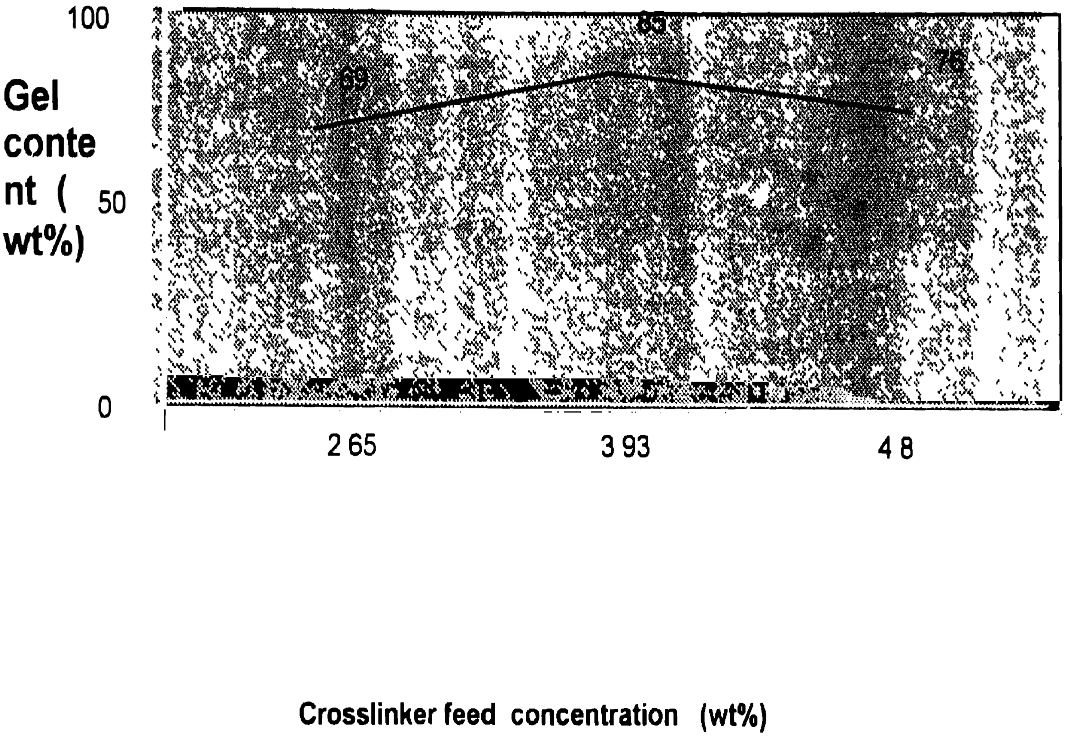
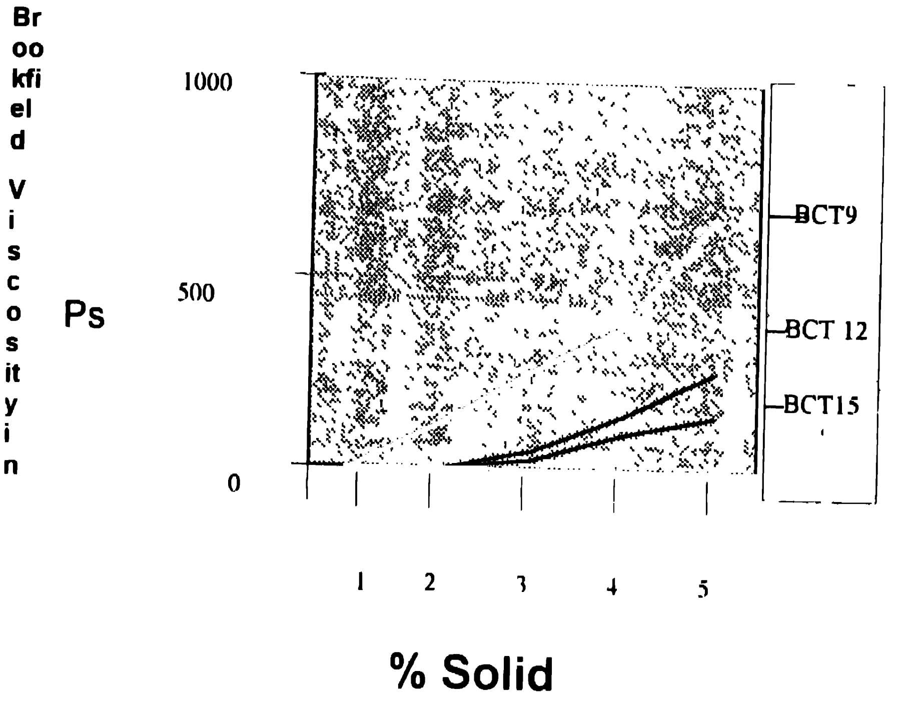


fig 3.4 Variation of Brookfield viscosity with solid content



Uncross linked polymer BCT 13 had viscosity 20 poise at 3.6 % solid content at 20 rpm pH (8.5- 9.5) where as the viscosity values of BCT 14, BCT 15, BCT16, BCT 17 were much higher at same solid content under similar condition On addition of ammonia cross linked polymers swell and remains in the form of gel , where as uncross linked polymers under go dissolution .

3.3.3.1 Effect Of Solid Content On Viscosity :-

On increasing solid content viscosity increases in all cases . According to the Bollmert [9] . The polymer chains in a solution are completely enveloped by the solvent and there is a critical concentration at which no free solvent is left . Above this concentration polymer chains are tightly packed together . BCT 9, BCT 12, BCT 15 are cross linked polymers , BCT 13 is uncross linked polymer . Cross linked polymers are giving rise to very high viscosity shown in **fig. 3.4**

Table 3.4

Solid %	Brook field viscosity in Ps		
	BCT9	BCT 12	BCT15
1.0	0.5	7	0.6
1.6	5.0	106	6.0
2.4	42.0	255	33.0
3.2	140	375	88.0
4.0	265	640	146.0

3.3.3.2 Effect Of Shear Rate On Brookfield Viscosity:

The drop in the viscosity values with increase in shear rate may be related to the break down of the hydrate or solvent enveloped network polymer in the dispersions by mechanical action which changes the structure from a gel to sol .[61] Subjecting the polymer solution to the mechanical stresses would separated loosely linked polymer coils leading to a drop in the viscosity shown in **table 3.5 and fig. 3.5**

Table 3.5 Effect of shear rate on brook field viscosity

RPM	Brook field viscosity			
	BCT13	BCT14	BCT15	BCT16
2.5	824	752	792	530
5	240	404	428	292
10	160	218	232	162
20	90	120	131	90
50	60	56	62	42
100	43	37	39	27

Solid content for the BCT 13 6.5 % , BCT 14 .BCT 15 and BCT 16 (3.6 %) and pH 8.3-9.5

3.3.3.3 Effect of the pH on the Brookfield Viscosity :-

Measurement of the Brookfield viscosity over a wide pH range (7 to 10 5) was carried out In all the cases viscosity was found to increase with increase in pH up to (9- 9 5) beyond that any increase in the pH to a drop in the viscosity **fig (3.6 – 3.9)** and **table (3.6- 3.9)**, Viscosity is related to coiled density of the polymeric chains , which is affected by a number of parameters such as molecular weight, number of carboxylic groups in the polymer chain and degree of dissociation On addition of ammonia to the polymer emulsion , same ionization occurs providing NH_4^+ (ammonium) counter ions and polymeric chains containing COO^- ions The negatively charged carboxylate ions will tend to agglomerate along the side chains , which repel each other electrostatically Causing extreme in enlargement of the polymeric coils giving rise to excessive increase of the viscosity After complete neutralization further addition of ammonia results in a build up of ammonium counter ions , leading to reduction of viscosity

fig (3.5) Variation of Brookfield viscosity with shear rate

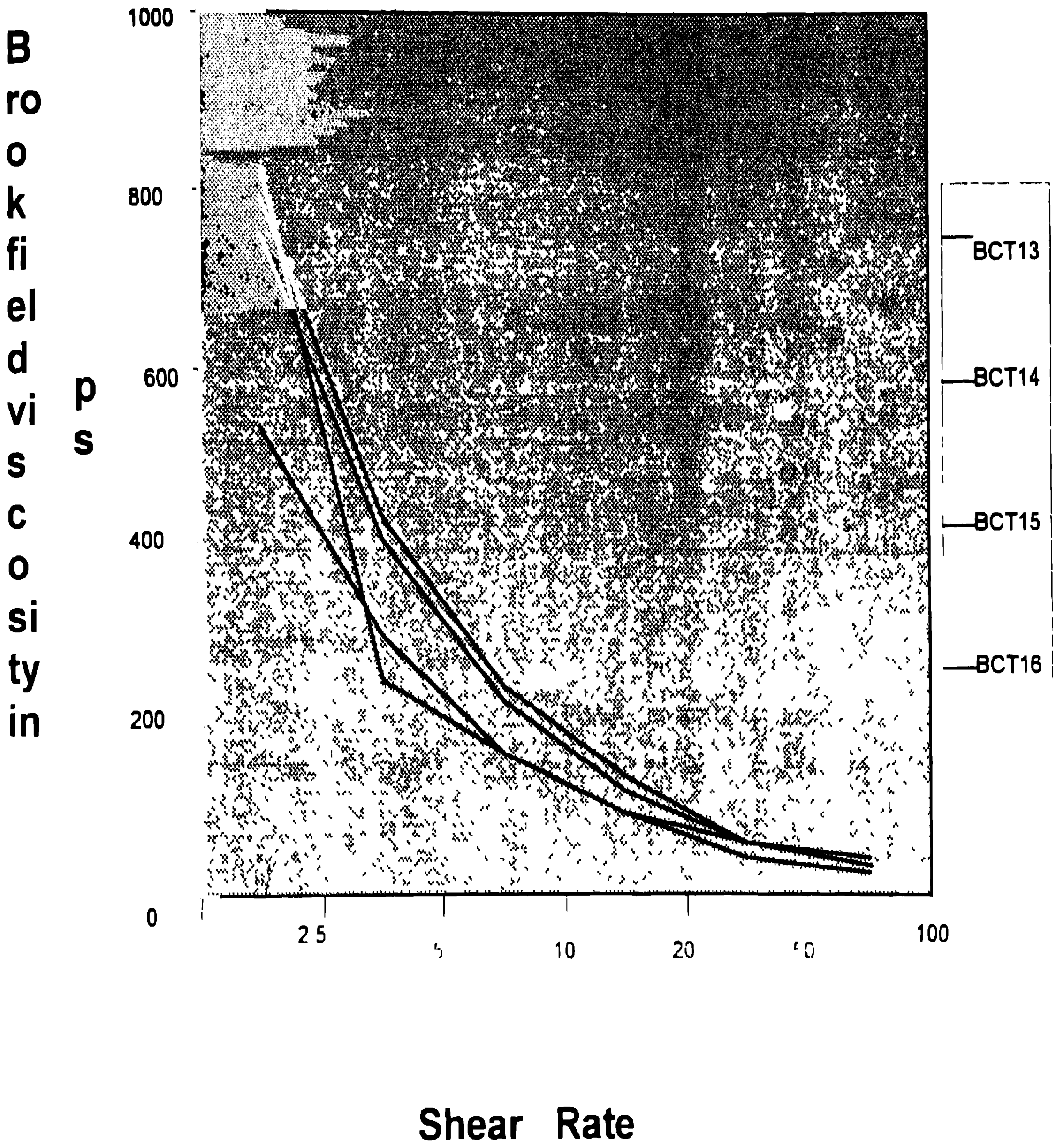


Table 3.6 – 3.9 variation of Brookfield viscosity with variation of pH at different shear rate.

BCT 13 Table 3.6

S.No.	RPM	Brook field viscosity in poise					
		pH 7.5	8	8.5	9.2	9.6	10
1	2.5	140	212	228	232	180	172
2	5	88	130	144	146	116	112
3	10	53	81	91	94	74	70
4	20	33	57	57	61	49	45
5	50	18	26	31	33	27	22

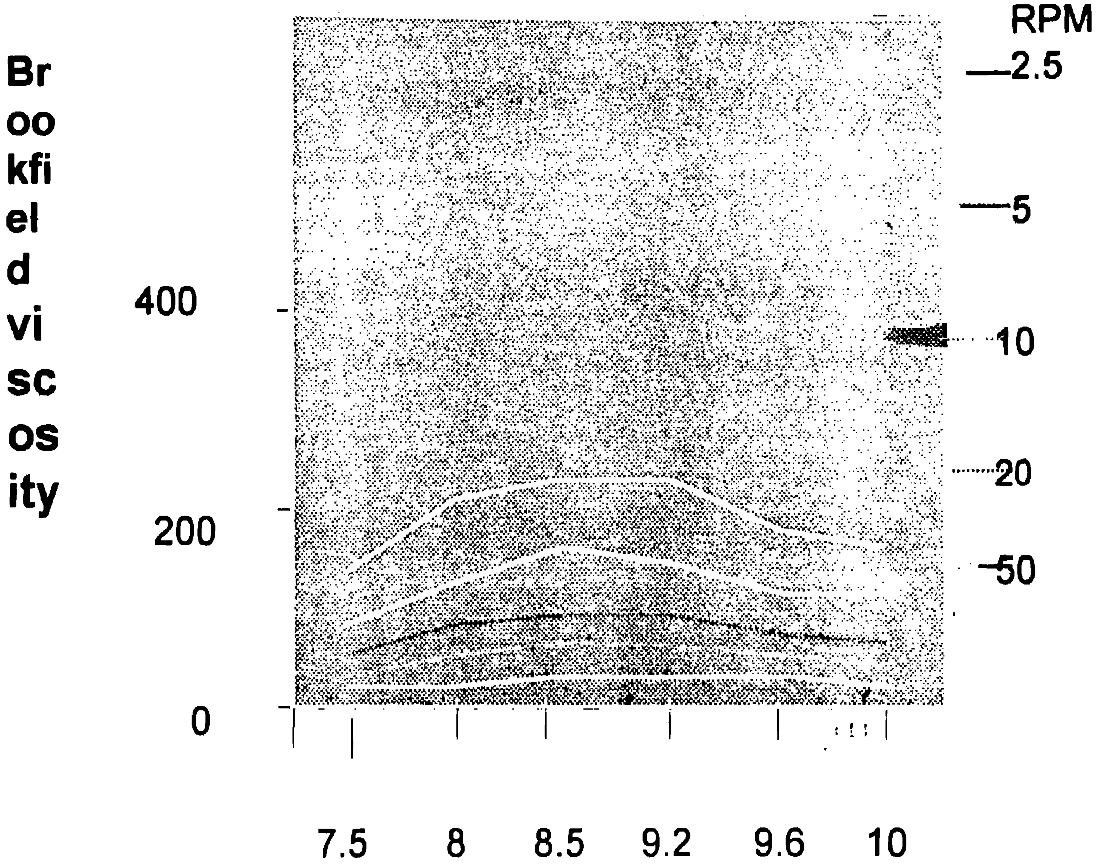
BCT 15 Table 3.7

S.No	RPM	Brookfield viscosity in poise					
		7.75	8.5	9.0	9.5	10	10.3
1	2.5	36	452	624	664	640	496
2	5	22	246	344	360	350	272
3	10	14	136	188	198	192	158
4	20	9	77	104	112	104	92
5	50	5	37	49	52	48	42

BCT 12 Table 3.8

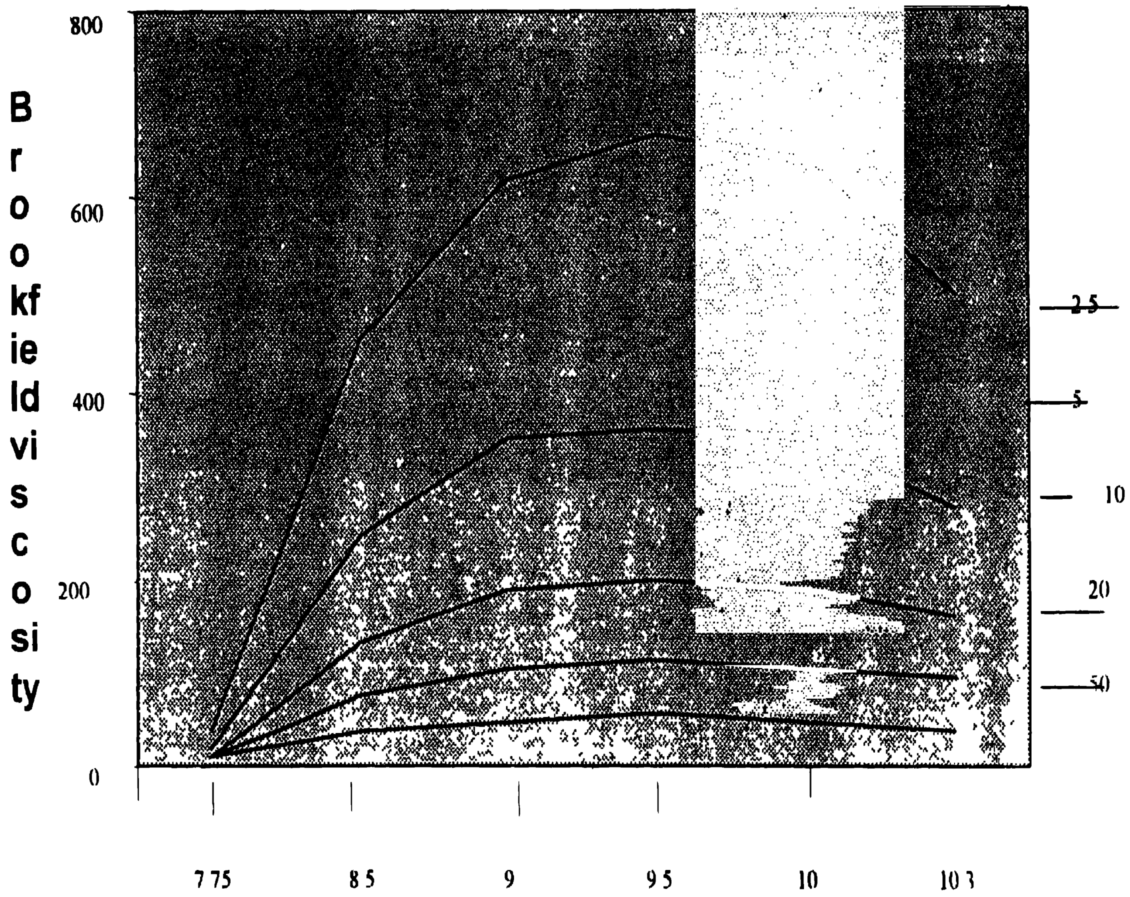
S .No	RPM	Brookfield viscosity in poise pH				
		7.2	8.3	9	9.5	10
1	2.5	848	1340	1360	1220	840
2	5	476	710	730	660	520
3	10	276	405	415	360	300
4	20	136	225	237	207	182
5	50	92	110	120	106	94

fig 3.6



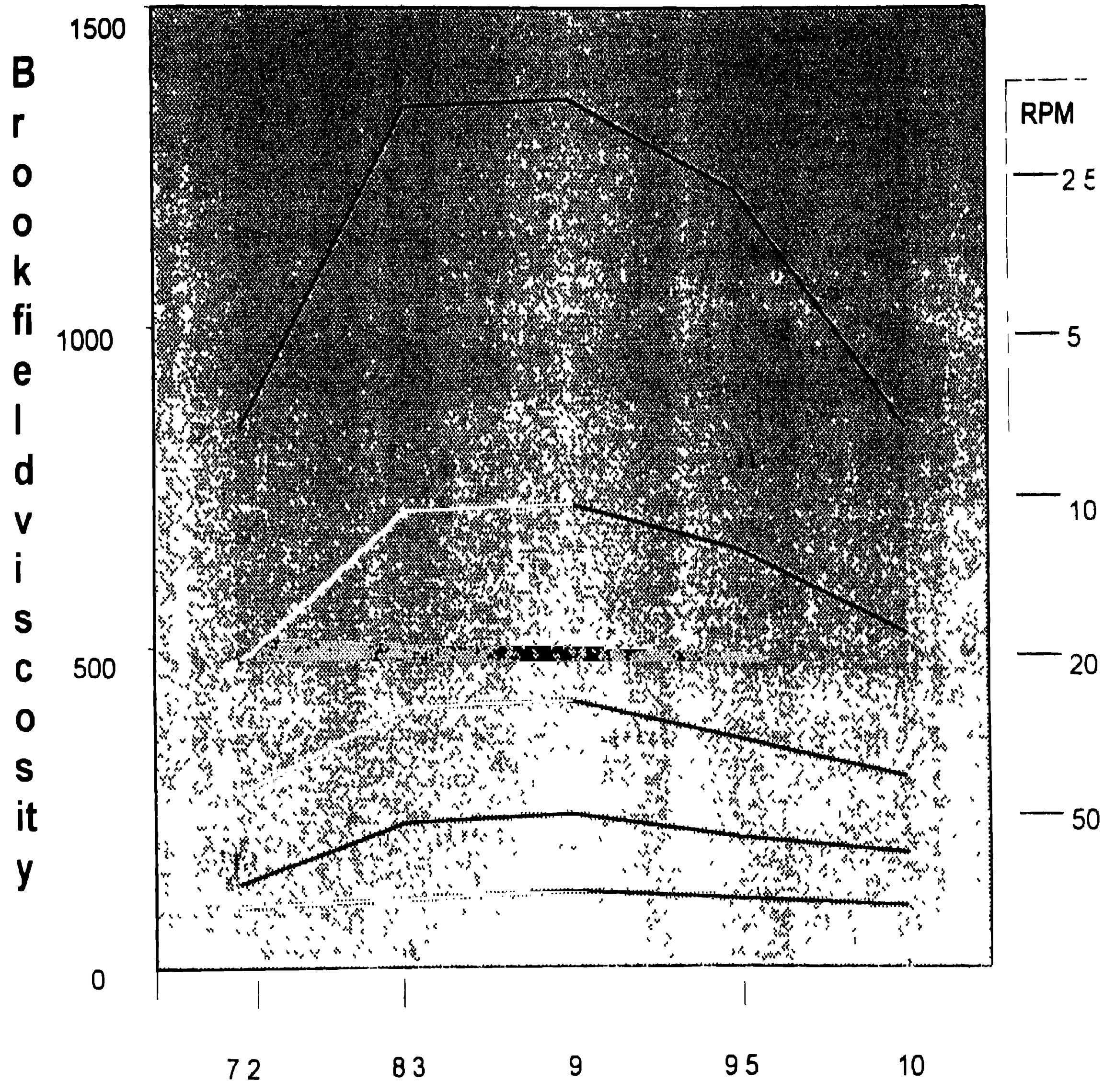
Effect of pH on Brookfield Viscosity of BCT 13 at different shear rate

fig (3.7)



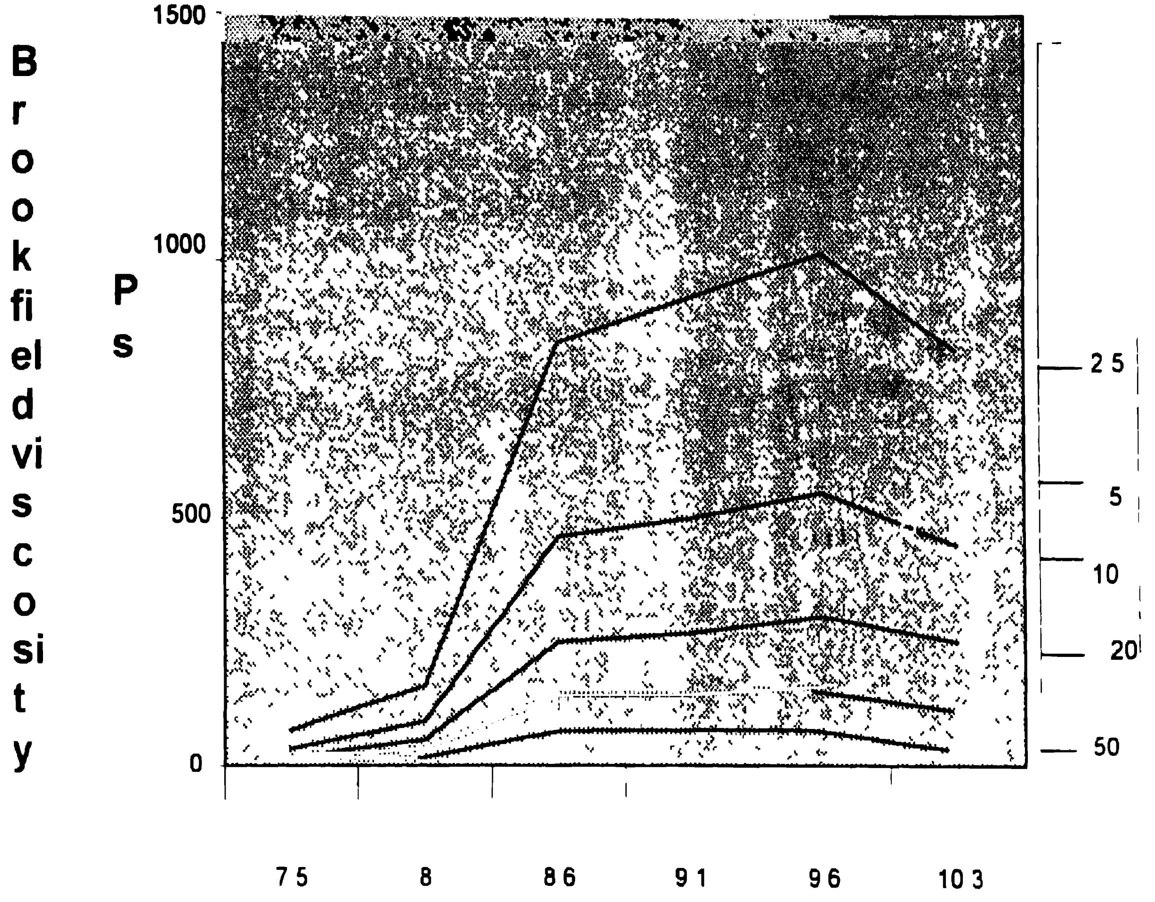
Effect of pH on Brookfield Viscocity of BCT15 at different shear rate(c=3.6%)

fig 3.8



Effect of pH on Brookfield Viscosity of BCT12 at different shear rate (c=3.6%)

fig 3.9



Effect of pH on Brook field Viscosity of BCT 9 at different shear rate (c=3.6 %)

BCT 9 Table 3.9

S.No	RPM	Brookfield viscosity in poise pH					
		7.5	8.0	8.6	9.1	9.6	10.3
1	2.5	75	156	848	928	1024	832
2	5	38	87	464	496	544	448
3	10	25	48	252	268	294	248
4	20	16	28	138	144	160	245
5	50	10	13	63	70	47	68

3.3.4 Storage Stability :

The storage stability of BCT 15 and BCT 13 was checked for 7 days at 24 hours interval and in general no change in viscosity was observed The good stability of these products may be due to the non biodegradability of synthetic polymers

Chapter

Performance
of
MAA-BA -EA Ter polymer
crosslinked
With
N Methylol methacrylamide
(MIMAM)

4.1 Introduction :

Pigments are molecular aggregates that are insoluble in all media , with which they came in contact during processing . They may belong to any class of chromopheres , but they do not possess any groups which can form bonds with fibres .Therefore pigments have no affinity for fibers and for their fixation , binding and fixing agent are required . The advantages of pigment printing are discussed in detail in chapter one .

A comparative study of the performance of different binders has been carried out by Teli [4] and Tull to identify the criteria which can be used in the selection of a binder for a particular set of conditions .

Curing of prints in pigment printing process is done at 150^{oC} . In case of kerosene emulsion thickener a catalyst is required for curing , because acidic pH is necessary to facilitate the requisite reaction between binder and side groups of fiber ($-OH$, $-NH_2$) . Di-ammonium phosphate catalyst (DAP) is used in kerosene emulsion thickener In case of synthetic thickener no such catalyst is required because during curing at such high temperature NH_3 goes away and the medium turned acidic required for fixation

4.2 Experimental :

4.2.1 Materials :

Cotton fabric was used for printing . It was scoured and bleached .

4.2.2 Printing auxiliaries :

TEX 2057 binder of VAM ORGANIC & CHEMICALS Ltd, CCL fixer based on melamine - formaldehyde Red FBR and Blue TFG pigments of Coluor Chem. Ltd and Yellow TGG and Black TBR pigments of Dye Star Chem. Ltd were used for printing . Di ammonium hydrogen phosphate $(NH_4)_2HPO_4$ was used as a catalyst in kerosene emulsion thickener .

4.2.3 Stock paste and print paste formulation :

Stock paste

Table 4.1 Kerosene stock paste (A)

Ingredients	Parts
Binder Tex 2057	10 0
Water	10 0
Urea	2 0
Kerosene	78 0
Total	100 0

4.2.4 Synthetic Binder Cum Thickener :

Several binder cum thickener were synthesized in chapter two Three of these e g BCT 9,BCT 12 & BCT 15 give satisfactory result like viscosity and film properties But

BCT 9 gives stiffness to the fabric and BCT 12 shows poor wash fastness and crock fastness, BCT 15 is the best of three in color shade, wash fast ness and in feel of fabric.

The solid content of BCT 15 prepared around 40.0 %. The stock paste was prepared by bring down the solid content to 3.6 % with the help of desired water and 25.0 % ammonium hydroxide solution was added to adjust the pH 8.5 - 9.5, pH was checked with the help of the pH system Model (Digital 361) of Elico India Ltd

4.2.5 Stock Paste of Commercial Thickener :

RAN 5000 is the indigenous thickener of RSA polymers and mostly used in India To prepare the stock paste of RAN 5000, 3 parts of the paste was added with a 86.5 parts water and left half an hour to swell

Table 4.2 Stock paste of BCT 15 (B)

Ingredients	Parts
Binder cum Thickener	9.0
Water	90.0
Ammonia(25.0%)	1.0
Total	100.0

Table 4.3 (C) Stock paste of partial substitution by kerosene

Ingredients	Parts
Binder cum Thickener	9.0
Water	85.0
Kerosene	5.0
Ammonia (NH_3)	1.0
Total	100.0

Table 4.4 (D) Stock paste RAN 5000

Ingredients	Parts
RAN 5000	3.0
Water	86.5
Binder Tex 2057	10.0
Ammonia (25.0%)	0.5
Total	100.0

Table 4.5 Printing pastes.

Ingredients	Kerosene emulsion	Binder cum Thickener & others (B.C.D)
Stock paste	100	100
Pigment (Red FBC , Blue TFG , Yellow TGG, Black TBR)	3 0	3 0
Fixer	1 0	1 0
Catalyst (33 0% soln) DAP	3 0	-
Total	107 0	104 0

4.2.6 Printing :

Samples are screen printed with two squeeze strokes followed by drying of the printed samples at 100 °C for three minutes and finally curing at 150 °C for five minutes

4.2.7 Partial Substitution by Kerosene :

Stock paste (C) was prepared by replacement of five parts of water from stock paste recipe of BCT 15(A) by kerosene oil given in table 4 3

Table 4.6 Chemical composition and code of Binder Cum Thickener and other thickeners used for pigment printing.

Thickeners and binder cum thickener	Effective solid content	Code
Binder cum thickener MAA wt % 21 93 EA wt % 37 4 BA wt % 36 6 MIMAM soln wt% 3 9	3 6	BCT 15
Commercial Thickener	1 1	RAN
Kerosene emulsion	0	KE
Five parts kerosene binder cum thickener	3 6	BCTKE

4.2.8 Evaluation of printed samples .:

The prints were evaluated in terms of color values, wash fastness, dry and wet crock fastness and feel of the fabric in terms of bending length .

4.2.8.1 Color value :

The color value of the printed samples was determined from front as well as from back (to determine the back penetration) by using Jaypack computer color machine system spectrophotometer . The color strength was expressed in terms of Kubelka munk function (K/S) .

4.2.8.2 Fastness Properties.

The wash fastness was tested using ISO test no 3 . The printed fabric was stitched with white piece of cotton fabric The sample was then subjected to washing using 5 gpl soap (surf excel) and 2 gpl sodium carbonate solution at 60 ^{oC} for half an hour in RGE wash fastness tester . It was then rinsed with cold water , dried at room temperature and evaluated with the help of Grey scale for change in depth of color and staining of white fabric . Dry and wet rub fast ness of the printed sample were determined using Shirley Crockmeter Tester . The sample was fixed to the rubbing device such that the long direction of the sample follows the track of the finger Crockmeter . It was rubbed back and forth ten times in a straight line . For wet rub fastness the rubbing cloths was wetted with water Samples were evaluated with the help of Grey scale for the staining of the . white fabric .

4.2.8.3 Feel of the Fabric :

Feel of the fabric was measured in terms of bending length on Eureka bending length tester The sample was cut to the size of bending length scale (6X1" size specimen"), place length wise on the plate form . The bending length scale was placed over the specimen such that the zero of the scale coincides with the bottom mark on the body of the instrument The scale was pushed forward gently and slowly

till the end of the sample was in line with two lines inscribed on acrylic sheets and the bending length was measured from the scale.

4.2.8.4 Viscosity Measurement :

The viscosity of various pastes was measured using Brookfield viscometer (Model R.V.D.T)

4.2 Results and Discussion :

4.3.1 Viscosity (stock and print pastes) :

Brookfield viscosity of all staok and print pastes were measured (at 20 RPM) and the values are given in table 4 7

Table 4.7

Sample code	Stock paste (Ps)	Print paste viscosity (Ps)			
		Red FBC	Blue TFG	Yellow TGG	Black TBR
KE	170	68	62	66	64
BCT 15	116	134	130	125	116
BCT KE	128	140	142	128	120
RAN	110	94	98	94	200

In BCT 15 Brookfield viscosity increases on addition of color for red, blue and yellow on other hand in RAN stock paste becomes gel on adding black color, high speed is required to get printable paste Brookfield viscosity increases dramatically with black color (110 to 200 Ps) RAN is not compatible with black color

4.3.2 Printing Performance of Binder Cum Thickener :

4.3 2.1 Colour value :

Colour value k/S of all the samples printed with Binder cum Thickener (BCT 15) including RAN 5000 were observed which was lower then kerosene emulsion thickener with all four pigments. Colour value is significantly affected by transparency of the thickener binder film Although the film of BCT 15 was clear than RAN 5000 , the decrease in colour value is observed due to foaming This foaming occurs due to presence of anionic emulsifier , which was incorporated during polymerization

Results of the k/S values from the printed samples are shown in figure 4 1

4.3.2.2Bending Length :

Bending length of the prints of BCT 15 was found highest **(table 4.8)** This is due to the residue left on the surface of the printed fabric of binder cum thickener This residue forms a film , which imparts stiffness to the prints When 5 parts replacement of water from BCT 15 by kerosene handle of the fabric improved

Table 4.8 Bending length of cotton printed with different thickeners and binder cum thickener .

Code	Pigments			
	Red	Blue	Yellow	Black
KE	2 7	2 71	2 03	2 05
BCT15	2 7	2 7	2 53	2 8
BCTKE	2 51	2 4	2 26	2 5
RAN	2 52	2 37	2 28	2 34

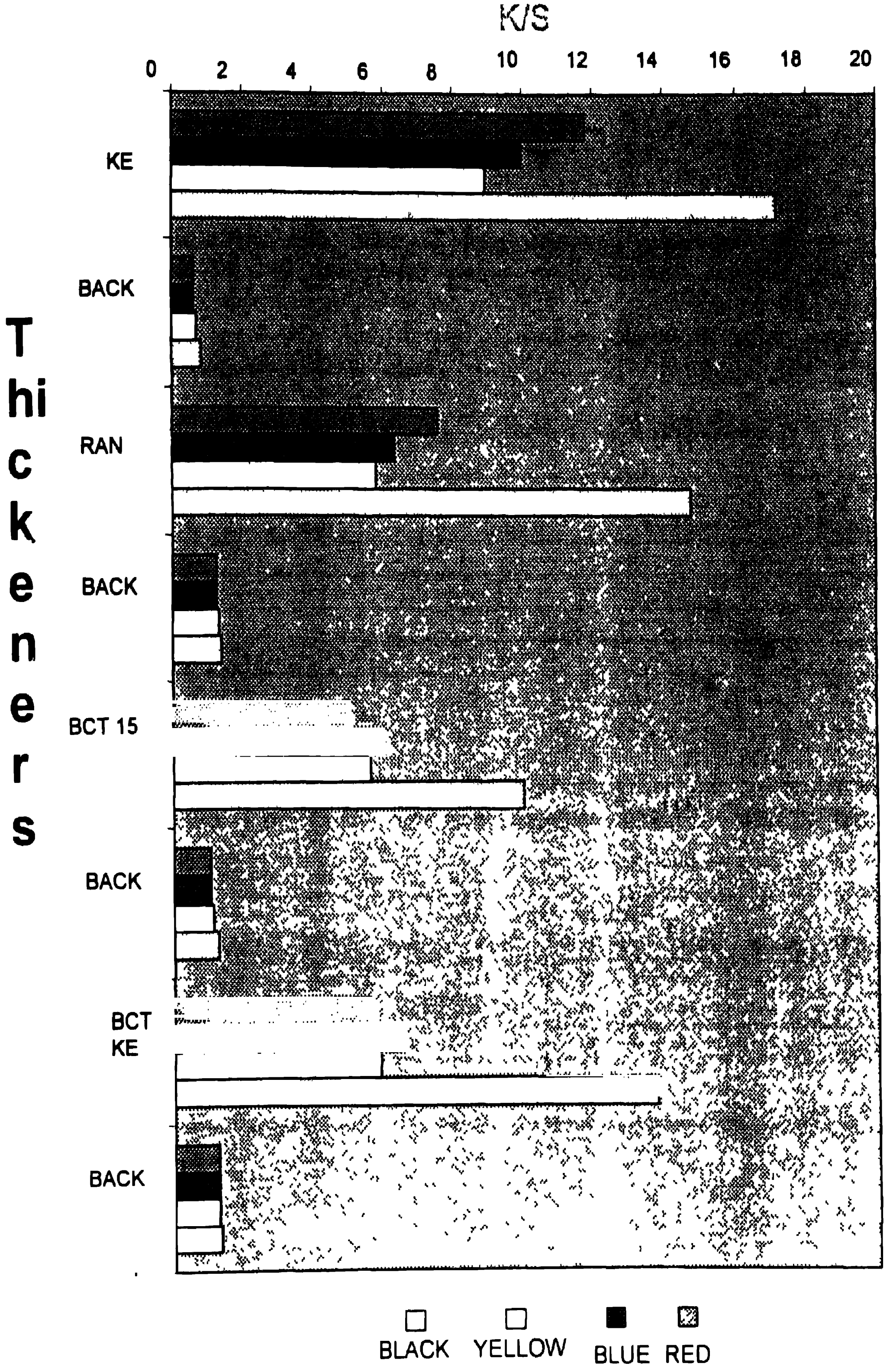


FIG 4.1 Colour value (K/S) of various with synthetic and kerose

4.2.3.3Fastness Properties :

Wash and rub (dry and wet) fast ness properties of the prints obtained from laboratory synthesized Binder cum Thickener BCT 15 were found almost similar to those obtained from KE and RAN .Crock fastness properties of BCT 15 give comparable results with KE and RAN . Wash fastness in terms of change of color came in 4- 5 on Grey scale in all cases.

Table 4.9 Effect of different thickeners on wash fastness .

Code	Grey scale reading			
	Red	**Blue**	**Yellow**	**Black**
KE	5	5	5	5
BCT 15	5	5	5	4
BCT KE	5	5	5	4
RAN	5	5	4	5

Table 4.10 Effect of different thickener on crock fastness properties (dry and wet) of samples printed with different thickeners .

Code	Grey scale reading							
	Red	**FBC**	**Blue**	**TFG**	**Yellow**	**TGG**	**Black**	**TBR**
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
KE	4	4	3-4	3	4	4	4	3
BCT15	4	3	4	3	4	4	4	3-4
BCTKE	4	3	3-4	3	4	4	4	3-4
RAN	4	3	3-4	3	4	4	4	4

Conclusions

Future scope of work

And

References

Conclusion and summary :

Methacrylic acid (MAA), butyl acrylate and ethyl acrylate co polymers and ter polymers were synthesized with varying percentage ratio of these monomers by emulsion polymerization technique . Alfox 200 , Spectra S301 and Sodium lauryl sulphate (SLS) were used as emulsifier . Potassium per suphate was used as the initiator . The rheological properties of the polymers have been studied . The performance of binder cum thickener in pigment printing has been reported with 4 pigments .The summary of the main findings discussed in previous chapter is given below

1 .Emulsion polymerization has done successfully with mixture of non ionic and anionic surfactants in the concentration of 7 2 wt % of total monomer

2 Polymers obtained were characterized for their moieties are using IR technique. The characteristic peaks at 1704 - 1734 cm -1 (vC =O), 1460 cm-1 (vC-CH3) , 1250 - 1170 cm-1 (vC-O) were observed in IR spectra The concentration of MAA from acidimetric titration was found low due to the in accessibility of the carboxylic group burried in side the particle core

3 As the degradation temperature of these polymers is above 180 oC Their application in pigment printing can be done as curing temperature is 150°C

4 On studying rheological properties it was found that cross linked polymers have higher viscosity than uncross linked polymers at same solid content Brookfield viscosity increased with increase in gel content N methylol methacrylamide as crosslinking agent provide 85 % gel content at 3 93 weight % concentration of total monomer

5 BCT 15 giving adequate viscosity and binding power was found to be 21 93 wt % of MAA, 36 64 wt % of BA , 37 43 wt % of EA and 3 93 wt % of MIMAM BCT 15 was selected for pigment printing due to adequate viscosity and ability to bind the pigment on the fabric

6 Brookfield viscosity of these Binder cum Thickeners are found to be sensitive to pH and shear rate The cross linked polymers yield higher viscosity at lower solid content than uncross linked polymers

7 Printing performance of Binder cum Thickener (BCT 15) with four different pigments (Red ,Yellow ,Blue and Black) has been evaluated, the results obtained were compared with kerosene emulsion thickener and commercial RAN 5000 The fast ness properties of the prints with BCT 15 gave comparable result with KE and RAN Feels of the fabric were lower from kerosene emulsion but almost equal to RAN

8 The film of BCT 15 was found more transparent than RAN 5000 with binder VAMTEX 2057

9 Colour value of prints with BCT 15 came lowest with all colours among the all cases in study The decrease in colour value was due to surfactants used in synthesis of BCT 15

10 In case of BCT 15 , 5 % replacement of water from stock paste recipe (BCT 15 A) by kerosene oil improved the colour value as well as feel of the fabric

Scope for Future Work:

1. Selection of surfactants in order to get stable emulsion at higher MA A content in the feed as well as to cause no damage to printing performance

2. Studies to increase the colour value specially in red and black colour

3. Studies to increase the solid content of the polymer emulsion than 40 %

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